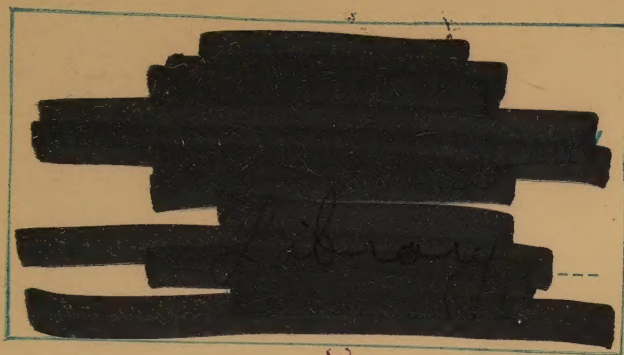


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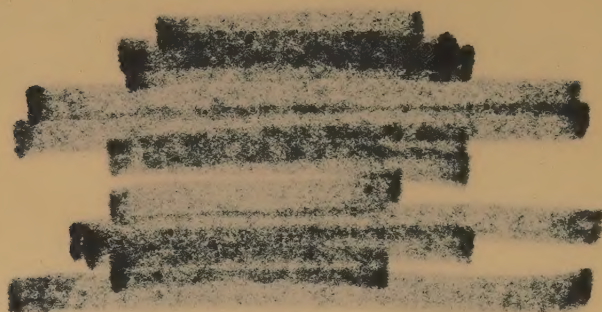
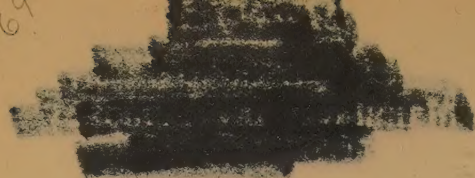
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STAINLESS IRON AND STEEL

STAINLESS IRON AND STEEL

BY

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TO MY WIFE

PREFACE

The publication of a book devoted entirely to the consideration of what is popularly supposed to be a single type of steel may at first sight need some justification. The popular notion as to the single character of stainless steel, however, is much more noteworthy for its persistence, in spite of propaganda to the contrary, than for its accuracy ! One of the main points of the author's work has been to emphasize the range of diverse materials included in the term "stainless steel" which permits such widely varying properties to be obtained from different types of this material. Such a wide range of materials and available properties is of great advantage to the potential user, more particularly the engineer, but it also entails the necessity of discriminating between various types of the steel in order that the most efficient use may be made of the material for any particular purpose. It has been the author's endeavour to present data pertaining to the various grades of the steel in as clear a manner as possible, in order to aid the user in making a choice of suitable grades for varying requirements.

One of the benefits of the modern study of metallography lies in the possibility it affords of indicating which treatments, thermal or otherwise, are likely to improve the properties of a metal and why such improvements occur. In the application of stainless steel, the study of the microstructure is of especial value as the observations indicate not only the cause of varying mechanical properties but also reasons why the materials offer varying resistance to corrosion. As it is desirable that the user of stainless steel should know how he may obtain the best qualities in this respect from the material he uses, the author has dealt rather fully with the microstructural characteristics of stainless steel; and in

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order that the account may be informative to those who have not specially studied metallography, he has endeavoured to write in the simplest terms.

It has been objected on more than one occasion that "stainless steel" is not a strictly accurate description of the qualities inherent in the material. One may quite admit this and agree that "unstainable," for example, would be a more appropriate name. "Stainless steel," however, has become so universally adopted as a designation of the materials described in this book that the substitution of another more accurate name would be a doubtful advantage.

The author is greatly indebted to Mr. F. G. Bell and Mr. R. Waddell, respectively Chief Engineer and Works Manager at Messrs. Brown Bayley's Steel Works, Ltd., for much of the information embodied in the last chapter; to Mr. H. Bull and Mr. A. Flint for assistance in proof-reading, and to all the members of his staff for help in preparing data, drawings, and photographs. He also wishes to thank the Directors of Messrs. Brown Bayley's Steel Works, Ltd., for permission to publish the data given in the book and, in particular, Mr. H. Brearley and Mr. M. R. Mainprice for much help and advice.

February, 1926.

J.H.G.M.

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INTRODUCTORY AND HISTORICAL

CHAPTER I

INTRODUCTORY AND HISTORICAL

The general rusting of iron and steel which occurs whenever these metals are left for any length of time either exposed to the atmosphere or to water, or buried in the ground, has been accepted almost as a matter of course. Thus it has been stated* "The tendency to rust is a characteristic inherent in the element known as iron, and will, in all probability, never be entirely overcome." Iron rusts and there is an end of it! If, owing to care and suitable protection, it is preserved over a long period of time, the achievement is looked upon as something out of the ordinary. It is recorded that when the first batch of stainless steel knives were being forged, the Sheffield cutler, on being told that the knives would not rust, expressed his opinion of such foolishness in strong "Sheffield," the meaning of which is quite unmistakable though the language is hardly printable.

This gradual corrosion of iron and steel entails enormous expense when considered in the aggregate. Everyone is familiar with its effects on various household articles and fittings, but the expense entailed by such corrosion is realised more easily when its effects on big engineering structures are considered. On the Forth Bridge, for example, painting is going on continuously from year end to year end. Estimates have been made, at different times, of the losses caused by the rusting of iron and steel work and, if a survey of the whole world is taken, the cost reaches very large figures. Thus, recently, in a paper read before the Royal Society, Sir R. A. Hadfield estimated that the annual cost owing to corrosion all over the world was well over £500,000,000. While such figures are possibly more in the nature of a guess, though probably guided by sound judgment, and hence only to be accepted with a considerable amount of reserve,

* "The Corrosion and Preservation of Iron and Steel," Cushman and Gardner, 1910.

they indicate that the annual losses due to the gradual corrosion of iron and steel reach enormous figures.

Apart altogether, however, from the question of expense, corrosion causes other troubles. In many engineering applications, the unsuspected corrosion of some part of, for example, a bridge may so seriously weaken the strength of the corroded part that it can no longer carry the load to which it is subjected and its failure, either by fracture or distortion, may have disastrous results on the whole structure. The trouble and loss of time occasioned by such breakdowns, apart from their cost, are serious items. For household and other purposes where polished fittings or utensils made of steel are used, the necessity of frequent polishing entails a considerable amount of work, which would be avoided if the surface did not corrode.

It is not surprising, therefore, that many efforts have been made to minimise or overcome troubles such as those mentioned above. In some cases, other alloys, such as for example those of copper, are used instead of steel or iron, owing to their superior resistance to general corrosion. There are many cases, however, apart from those where the extra expense of such resistant alloys would have to be taken into account, where the mechanical properties desired can be obtained only by the use of some type of ferrous metal. In such cases, if a bright surface is required, either a considerable amount of energy must be expended at frequent intervals in polishing the article, with consequent wear of the latter, or else it must be covered with some type of transparent varnish or lacquer. Obviously the latter method cannot be applied in many cases. A metallic surface more or less permanent in character may also be obtained by tinning or galvanising or by electro-plating with some metal which is resistant to a greater or less extent to corroding agencies. When a polished or metallic surface is not necessary, there are other methods of protection available, such as painting, covering with an adherent coat of magnetic oxide of iron (e.g., by the Bower Barff process or its modifications or by the Ruffington process) or the production of a phosphatic coating such as that obtained by the Coslett process.

All such methods, while of great value for many purposes, have obvious disadvantages in certain important

respects. In some cases the coating produced is brittle and, therefore, liable to chip off, while in all cases the application of the protective coating must be the last stage in the manufacturing process ; no further drilling, sawing or any other type of machining should be done after the coating is applied, or the continuity of the latter is broken and an unprotected surface of the iron or steel exposed. From an engineering point of view, however, an even more serious drawback is that the protection is entirely superficial in character and is, therefore, of little lasting value if the article to which it is applied is subjected during use to any type of rubbing or wearing action or if a cutting edge is required. In such cases the method employed to render the iron and steel satisfactorily resistant to corrosion must not be confined to the surface only, but must be incorporated in the body of the material so that, as the outer surfaces are worn away, the new material exposed shall be equally resistant. Such a type of protection can only be effected by altering the properties of the whole mass of the steel and the only possible way of doing this is by alloying the steel with some other metal which shall have the power of preventing the alloy produced from being attacked by corrosion.

The possibility of retarding the corrosion of iron and steel by the addition of other metals has been recognised for many years and some alloys having marked resistance to corrosion were discovered a number of years ago. Probably the best known examples of this are the high nickel steels, containing 25 to 35 per cent. nickel. Such material, though by no means incorrodible, resists corrosion to a very much greater degree than ordinary steel and has been used to a considerable extent. It is, however, rather expensive and its mechanical and physical properties are not suitable for all purposes ; for example, it cannot be hardened by quenching or by any other form of treatment which can be applied to an article possessing approximately its final shape and dimensions, while in no case can it be given a hardness value anything approaching that required for a cutting tool.

Another material having resistance to a special form of corrosion, which may be referred to, contains about 12 or 14 per cent. of silicon and is sold under various trade names. Such material has very great resistance to the attack of mineral acids. Owing to its nature, however, it is more or

less allied to cast-iron, hence its use is restricted to purposes for which its mechanical and physical properties are suitable, thus it is comparatively brittle and it cannot be forged or rolled.

It will be seen, therefore, that there is an immense field for a steel product which possesses the property of great resistance to corrosion in each and every part of the articles which may be manufactured from it, and which also has a wide range of physical and mechanical properties comparable in extent with those found in the range of material known to-day as "steel." Such a non-corrosive material is now available in the form of "Stainless Steel."

Stainless steel was first introduced to the public in 1914 in the form of table cutlery and its almost exclusive use for cutlery purposes for a considerable period of time after that date has led to the belief, probably widely held, that stainless steel is simply a special type of cutlery steel with a very limited range of mechanical properties. It has even been considered to be a special form of plating. If this were so, stainless material would have a very limited application and would not be of great interest to engineers. Fortunately, however, this is not the case. Stainless steel is really a whole series of steels, whose mechanical and physical properties vary widely in a similar manner to the variations met with in the different varieties or "tempers" of ordinary carbon steels, but which all have the distinguishing property of great resistance to corrosion conferred on them primarily by the presence of a considerable percentage of chromium. As a general rule, the amount of this element present in stainless material is in the range 11 to 14 per cent.

In ordinary steels, variations in the mechanical properties of the material are controlled largely by the presence of varying amounts of carbon; thus very mild or soft steel may contain 0.10 per cent. carbon or less, while for certain types of tool steel 1.6 to 1.8 per cent. is occasionally added. These values represent extremes and intermediate amounts are chosen to give properties suited for definite purposes. So in stainless steel, variation in mechanical properties is brought about largely by the presence of varying amounts of carbon; in this case, however, the range of carbon content, for reasons which will be seen later, is much more restricted so that, as a general rule, the carbon content

of stainless material is not more than about 0.4 per cent. Stainless steel, also, frequently contains small amounts of nickel, up to about one per cent.; the presence, however, of such amounts of this element, which are not purposely added, but are there accidentally, has no appreciable influence on the non-corrodibility of the steel.

The resistance to corrosion of such high chromium steel was discovered by Mr. Harry Brearley in 1913. Mr. Brearley was at that time chief of the Research Laboratory run jointly by Messrs. John Brown & Co., Ltd., and Messrs. Thomas Firth & Sons, Ltd., Sheffield. He was at the time engaged on an extensive research on the resistance to erosion of various steels in reference to their use for rifles and naval guns. Among the steels examined for this purpose, were some containing large amounts of chromium. In the course of these investigations, numbers of samples, in different conditions of heat-treatment, were examined microscopically as is, of course, usual in such investigations. In carrying out this examination, Mr. Brearley noticed that these high chromium steels were either not etched at all or only attacked very slowly by the usual reagents used for etching the polished surfaces of sections of steel prepared for microscopic examination and that, moreover, they did not rust when exposed for considerable periods to the atmosphere of the physical laboratory. He also found that, both with the usual microscopical reagents and also with new types developed for the purpose, the same steel under different conditions of heat treatment would sometimes etch and sometimes not etch. He was at once struck with these marked characteristics and proceeded to investigate, on the one hand, the limiting ranges of composition for producing a steel practically resistant to ordinary corrosion and also the conditions of heat treatment necessary with any particular steel for developing to the greatest extent this resistance to corrosion.

The many possible uses of such a material having very great resistance to corrosion were evident to Mr. Brearley, and one of the most obvious purposes where it was likely to be very useful was that of cutlery. At first there was some difficulty in getting the material tried but eventually, about the middle of 1914, Mr. Brearley was able to persuade Mr. E. Stuart, cutlery manager for Messrs. R. F. Mosley, of Sheffield, to work up some of the steel into knives. The

results were strikingly successful in spite of initial difficulties, due largely to the best conditions of forging and working the steel being different from those of ordinary cutlery steel. In this respect very great credit is due to Mr. Ernest Stuart for the unremitting efforts he made to adapt the processes of knife making to the unusual qualities of the steel and to Messrs. R. F. Mosley for realising the possibilities of the material and possessing such confidence in it as to allow their works to be used for this pioneer experimental work.

Early in 1915, Mr. Brearley severed his connection with Messrs. Brown's and Firth's and became Works Manager at Messrs. Brown, Bayley's Steel Works, Ltd. Owing partly to lack of time due to pressure of work in his new position and for other reasons, no application was made for a British patent, but in August, 1915, a patent was granted in Canada, followed in September, 1916, by a further patent in the United States of America, for a stainless article which owed its special stainless properties to three novel features ;

- (a) That its chemical composition was within certain well-defined limits ;
- (b) That it had been heat-treated to produce certain microstructural characteristics ;
- (c) That it was metallically clean and in an undistorted condition.

The texts of these two patents are given in the Appendix from which it will be seen that the range of composition specified was 9 to 16 per cent. of chromium with carbon below 0.7 per cent. and preferably below 0.4 per cent. Certain other elements in limited amounts, up to 1 or 2 per cent., were also allowed as not affecting the result, the elements actually specified in the patents being nickel, cobalt, copper, tungsten, molybdenum and vanadium. The U.S.A. patent applies more particularly to cutlery and other polished articles, while the Canadian patent especially embraces material which has been hardened and then tempered to a sufficient extent to be tough and ductile.

The statements made in the patents with respect to the absence or presence of "microscopically distinguishable free carbides" relate, as will be seen later, to material hardened from a fairly high temperature. The inventor

does not state how he arrived at this demarcation in the carbon content but it seems possible that the value of 0.7 per cent. carbon was estimated from the appearance of small samples cooled from a molten condition. At that time, however, the microstructure of high chromium steel and the complexities of its heat treatment were not fully understood. The range of composition specified, however, does mark out wonderfully well the material useful for technical purposes and it is highly probable that, had the composition of stainless material to be fixed at the present time with the accumulated knowledge of the past few years at the disposal of the discoverer, the range chosen would not differ materially, if at all, from that laid down ten years ago.

The production of a chromium steel was not by any means new, in fact the literature of iron and steel metallurgy during the nineteenth century and the first ten years of the present century contains many references to the preparation of chromium steels and to some of their physical properties. Several comparatively extensive investigations into the properties of chromium steels had been carried out, notably those of Hadfield, Guillet and Portevin, but the remarkable point is that neither these investigators or any others appear to have had any idea that high chromium steels were so remarkably resistant to corrosion. In most cases, no study of the effect of chromium on the rate of corrosion had been made, while in one notable case in which such experiments were carried out, though to a very limited extent, that of Hadfield,* the results indicated, as will be seen later, that the rate of corrosion increased with increasing content of chromium. It is not necessary to give a detailed account of the many investigations on chromium steels which do not deal in the slightest degree with the effect of this metal on the corrodibility of the steel. For those interested in the early history of chromium steel, a good summary of such investigations will be found in Hadfield's paper mentioned above. It is of interest, however, to review briefly the few papers or articles in which some reference is made to corrosion or to the resistance of the metal to attack by acids.

The earliest reference, with which the author is acquainted, to the influence of chromium on the corrodibility of iron or to the rate of its solution in acids is in an article by

* *J.I.S.I.*, 1892, II, 48.

Berthier,* dealing with alloys of chromium with iron and with steel. Berthier stated that ferrochromium is much less readily attacked by acids than iron, the more so the more chromium it contains. The next one in order of date appears to be a paper by Robert Mallet†, on "The Action of Water on Iron," in which he states that alloys of iron with any of the following elements, nickel, cobalt, tin, copper, copper and zinc, mercury, iridium, osmium, columbium, and chromium are less corrodible than iron, and of these alloys that of chromium is least corrodible. He states, however, "with a metal positive to it (like chromium), though it may possibly protect the iron from action, will, by its own removal, be likely to render its texture open and coarse and, hence, more fitted for its subsequent solution and removal." It appears as if Mallet's idea was that the resistance to corrosion of iron containing chromium was, at the commencement of exposure, increased by the presence of the chromium, but that the chromium was first removed by the corroding agency and that after this had occurred the remaining iron would be more quickly corroded than if the chromium had not been present.

Mallet also states that Faraday had found that the alloys of most of the metals with steel which he had tried were much less acted upon by moist air than steel unalloyed.

In an article by Fremy‡ on crystallised chromium and its alloys, it is stated that "Chromium crystals resist the action of the strongest acids and even of aqua regia." Fremy also remarks that he has noticed alloys of chromium frequently resist the action of concentrated acids. The greater resistance of iron-chromium alloys to attack of acids as compared with that of iron was also noted by Boussingault.§

Gruner studied the capacity of resistance of various steels to the influence of air, sea-water and acids. His opinion on a chromium steel is summarised at the end of the report in the following words: "The presence of chromium favours corrosion by acidulated water as well as by humid air and sea-water."

* *Annales de Chimie et de Physique*, 1821, Vol. 17, p. 55.

† B.A. Report, 1838, Vol. VII, p. 265.

‡ *Comptes Rendus*, 1857, Vol. 44, p. 632.

§ *J.I.S.I.*, 1886, II, 807.

|| *Annales des Mines*, 1883, I.

In 1892, R. A. Hadfield published the results of an extensive investigation on chromium steels* which also included a few corrosion tests. These latter, however, were carried out by exposing the samples to the attack of fifty per cent. sulphuric acid, the assumption being made apparently that such an acid test would give results in the same order as those given by ordinary corrosion tests but at a greatly accelerated rate. Hadfield's results showed that as the chromium rose from 1·18 per cent. to 9·18 per cent., the rate of attack increased very decidedly. It is noteworthy that Hadfield does not comment in his paper on these results nor does he refer to any other corrosion tests. In an Appendix to Hadfield's paper, Osmond contributed a description of the microstructures of some of Hadfield's steels. He noticed that in those containing 5·19 and 9·18 per cent. chromium, the microstructure, in some cases, showed the presence of minute particles, presumably carbide, which were not attacked in the least by the etching reagent used, 20 per cent. nitric acid.

What appears to be the only reference to the relative effect of carbon and chromium on the resistance to acid attack of iron alloys is contained in an article by Carnot and Goutal, "On the Condition of Silicon and Chromium in Metallurgical Products."† These investigators found that chromium steels containing a small amount of chromium are readily attacked by acids (even when cold and diluted) if they are highly carburised, but much more slowly and with greater difficulty when they contain a small amount of carbon.

Hadfield's results as to the increased corrodibility of chromium steels in sulphuric acid were confirmed by Monnartz‡, who also found similar results with hydrochloric acid. Monnartz also found that the behaviour of chromium steels with respect to nitric acid was more complex. Up to 4 per cent. chromium, the resistance to dilute nitric acid decreased as the chromium increased, while, on the other hand, the resistance to concentrated nitric acid increased. Above 4 per cent. chromium, the resistance to dilute nitric acid rapidly increased as the chromium rose to 14 per cent. and more slowly afterwards, until at 20 per cent. chromium

* *J.I.S.I.*, 1892, II, 48.

† *Comptes Rendus*; 1896, Vol. 126, 1243.

‡ *Metallurgie*, Vol. VIII, 1911, p. 161.

the alloys were as stable as pure chromium. Monnartz' work was concerned mainly with the resistance of the alloys to acids. He mentions, however, that the higher chromium alloys, especially those containing over 40 per cent. chromium, showed excellent stability towards atmospheric conditions. Thus he states that such alloys, which were exposed for two years to the influence of the laboratory atmosphere, showed no trace of change, retaining their original bright lustre. They were also stable in a remarkable manner to river-water; in addition, the high percentage alloys resisted cold sea-water well, while those containing less chromium were attacked. Monnartz, however, does not give any details as to which alloys (his series included alloys up to 98 per cent. chromium) were or were not successful; in fact the remarks as to atmospheric and water attack are introduced almost casually at the end of the section of the article dealing with the resistance of the alloys to nitric acid.

Finally the corrodibility of a series of steels containing up to 5.3 per cent. of chromium (along with other alloy steels) was examined by Dr. Newton Friend,* who found that his results confirmed those of Hadfield as to the resistance of such steels to the attack of sulphuric acid. As regards the resistance to neutral corroding media, he states that in such media "the resistance offered to corrosion apparently rises with the percentage of chromium. This is particularly the case for salt water, and the employment of chromium steels in the construction of ships would appear to be fully justified on this ground alone." In connection with this, it should be noted that Friend did not experiment with any steel containing more than 5.3 per cent. chromium, an amount quite insufficient to reduce the corrosion of the steel in neutral media to negligible amounts and that, although he found the amount of corrosion to be considerably reduced by the presence of this content of chromium, such steels still corroded to a quite considerable extent.

It will thus be seen that at the time of the discovery of the remarkable non-corrosive properties of the material subsequently known as "stainless steel," the published information on chromium steels would not have led anyone to suspect that such remarkable properties were likely to

* *J.I.S.I.*, 1912, I, 249; 1913, I, 388.

be present. Broadly speaking such knowledge as there was indicated that :—

- (a) Iron-chromium alloys containing large amounts of chromium resisted the attack of certain strong acids.
- (b) The addition of chromium decreased the resistance of steel to the attack of sulphuric acid. It should be remembered that such tests were believed to indicate the general corrodibility of the several steels in other media, and hence gave the impression that chromium steels were not likely to be of much value as non-corrosive materials.
- (c) It had been shown that the presence of chromium up to about 5 per cent. retarded the corrodibility in neutral media. The investigations, however, did not indicate the influence of the carbon content, nor of the heat-treatment of the steel (or of other points which, as will be shown later, have a decided influence on the non-corrosive properties), nor did they suggest that it was likely that a steel practically immune from corrosion could be developed.
- (d) Monnartz' work showed that "high chromium alloys" (especially those with 40 per cent. chromium and upwards) resisted atmospheric attack and river and sea water.

It is therefore clear that the discovery of the non-corrosive properties of stainless steel by Brearley, in 1913, was something entirely new in the history of chromium steels and apparently quite unknown to any previous investigator on such steels.

At the time of the discovery of stainless steel, there were several varieties of ferrochromium on the market, the variable being the carbon percentage. Chromium has a very great affinity for carbon so that it is a matter of some considerable difficulty to produce alloys rich in chromium and, at the same time, comparatively free from carbon. In the grades of ferrochromium generally available at that time the carbon ranged from about 8 per cent. to about 0.6

or 0·8 per cent. As such alloys contained about 60 per cent. chromium it is obvious that only the lowest carbon material was of any value for producing a low carbon steel containing about 12 per cent. chromium and also that with this lowest carbon ferrochromium, the commercial production of a stainless steel with less than about 0·25 per cent. carbon was impossible while it was quite easy for the carbon to rise to 0·3 or 0·4 per cent. during melting, owing to the avidity with which the molten material absorbed carbon.

There were certainly carbonless chromium alloys and even metallic chromium on the market ; these alloys, which were produced by the Thermit process, were, however, much more expensive than the other chromium alloys and they were not being produced in any quantity. As it happened, however, the carbon content of the stainless steel produced by such low carbon alloys as are mentioned above, i.e., in the neighbourhood of 0·3 per cent., was probably the most suitable for the production of stainless cutlery for which the material was first used commercially, so that the need of lower carbon material was not at the time urgent. Any further development in that direction which might have taken place was held up during the period of the Great War, because the value of stainless steel for war purposes, particularly for the manufacture of valves for the engines of aeroplanes, was soon realised, with the result that the whole of the output of stainless steel was taken for war purposes. Here, again, there was no particular incentive to produce a lower carbon material because, for the manufacture of aero valves, a somewhat higher carbon steel than that used for cutlery was an advantage for reasons which will be seen later. After the conclusion of hostilities, however, opportunities occurred for developing the production of stainless steel with carbon content considerably below 0·3 per cent., and with the advent, on a reasonable commercial scale and at an economic price, of carbonless ferrochromium, the production of stainless material with 0·1 per cent. carbon or less became possible. As far as the author is aware, such low carbon stainless steel, or stainless iron as it is quite generally called, was first produced on a commercial scale in June, 1920, when the firm with which he is associated made a five or six ton cast of material containing 0·07 per cent. carbon and 11·7 per cent. chromium and cast it into twelve-

inch square ingots. Such low carbon material had certainly been produced prior to this, but only in small quantities and generally for experimental purposes only.

The physical and mechanical properties of the low carbon material thus produced were found to be ideal for a number of purposes. Thus it could be hot worked with considerably greater ease than the ordinary stainless steel and, after suitable heat-treatment, it gave a range of tensile strength of the order of 35 to 70 tons per square inch and was, therefore, suitable for many purposes for which the higher tensile strength of stainless steel had been rather a disadvantage.

The necessity for using a totally different raw material, carbonless ferrochromium instead of the ordinary low carbon variety (0.6 to 1.0 per cent. carbon), has led to the idea that stainless iron is a distinct product and quite different from stainless steel. While this may, perhaps, be true in some respects, it is quite wrong metallurgically. The name stainless iron may be commercially justifiable, but the material is more correctly described as a very mild stainless steel and forms the lowest carbon member of a series of steels of continuously varying carbon content which are, in many respects, analogous to the series of ordinary carbon steels ranging from "dead soft" to tool steels, except that in the case of the stainless material the range, as mentioned earlier, is not so extensive. Thus it is not yet possible to prepare stainless material with a tensile strength of the same order as that of the softest carbon steels, i.e., about 25 tons per square inch, while at the other end of the scale it is only possible to produce the same degree of hardness in stainless steel as is associated with a fully hardened carbon tool steel by increasing the carbon content to a value which entails a considerable loss in resistance to corrosion. However, within the limits of tensile strength most satisfactorily available, which extend from about 30 tons per square inch up to about 110 tons per square inch, stainless material of any strength may be produced by suitably varying the composition and treatment of the steel.

The idea that there are different "tempers" of stainless material similar to those of ordinary carbon steel is not yet by any means fully realised, especially in the engineering industries. This is unfortunate as, generally, the use of the proper type of stainless material for a particular

purpose is as important with this material as it is with ordinary carbon steel.

It may be interesting in this connection to quote from an article on Stainless Steel contributed by the author to the *Journal of the Society of Chemical Industry*, in November, 1920. In the closing paragraph of that article the author stated "Just as in the far-off days 'steel' was regarded as a hard product of iron, and little or no attempt was made to grade it into harder or softer varieties, so at present stainless steel is, to most people, a product having only one distinct set of properties, many regarding it solely as a special type of cutlery steel. In times gone by, as the use of steel became more general, it was realised that by varying the content of carbon or manganese, steels of widely-different intrinsic hardness could be produced, and for each purpose some definite 'temper' of steel was best suited. In the same way, as the use of stainless steel becomes more general it will be found that products of different intrinsic hardness (corresponding to the varieties of ordinary steel) can be produced, all of them having the distinguishing property of great resistance to corrosion, but varying among themselves as soft or mild steel differs from file steel. For each use of stainless steel there will be an optimum 'temper.'"

THE INFLUENCE OF CHROMIUM ON THE
STRUCTURE AND HARDNESS OF STEEL

CHAPTER II

THE INFLUENCE OF CHROMIUM ON THE STRUCTURE AND HARDNESS OF STEEL.

The development of the science of metallography during the past thirty years or so has enabled metallurgists not only to evolve improved methods for the manufacture and treatment of steel but also to give a logical explanation of many of the practices which had been previously evolved in a purely empirical manner by skilled craftsmen who have built up so much of the art of steel making. In the case of alloy steels, the study of the structure and constitution of the steel and the influence of the progressive addition of the alloying elements on this structure and constitution has been of fundamental importance both in the development of the steels themselves and also of the heat-treatment most likely to bring out the special characteristics of the several steels. It is well known that the properties of ordinary steel can be varied over a wide range by varying the composition of the steel, mainly, of course, with regard to carbon, and also that the properties of any given steel can be altered by subjecting it to various treatments, either mechanical or thermal or both combined. In addition to affecting the physical properties, such as hardness, toughness, ductility, etc., of the metal, these varying compositions and treatments leave their mark on its structure, so that it has been one of the aims of the metallurgist to follow these changes in the structure and correlate them with the corresponding changes in the physical properties.

The early development of some of the alloy steels occurred at a time when metallographical investigation had not attained the prominence which it now holds in the iron and steel industry and when the fundamental principles underlying the correct heat treatment of steel were not appreciated or even understood. As a consequence, such

alloy steels as were used were, more often than not, employed in a condition in which their useful properties were not by any means fully developed ; owing to this, more expensive steels were used to obtain desired properties than were actually necessary. In the light of modern knowledge, some of the older investigations on such alloy steels and the accounts of the heat treatment suggested for these, form very curious though interesting reading.

In the case of stainless steel, knowledge of the changes produced in the internal structure of the metal by varying composition and treatment is of exceptional importance, because, in this case, not only do the ordinarily observed physical properties vary with such changes, but also the degree of resistance to corrosion. In order that the most efficient use may be made of stainless steel, the effects of such changes in composition and treatment must be thoroughly appreciated. Hence, a knowledge of the changes produced in the structure and constitution of the steel by different thermal and mechanical treatments and of the fundamental principles which underlie the metallographical explanation of these changes is very helpful not only to the manufacturer but also to the user of the steels. For this reason the author makes no excuse for dwelling at some length on the metallographical aspect of the subject. He believes that a general acquaintance with this aspect will be of great assistance to those who wish to take advantage of the almost unique properties of the steel and in order that it may appeal to those whose knowledge of modern metallography is limited, he has endeavoured to write in the simplest terms.

The addition of large amounts of chromium to steel produces a number of characteristic effects on the properties of this metal. Of these effects the four following are of particular interest from the point of view of structural characteristics and heat treatment. The presence of chromium in steel :

- (a) Lowers the carbon content of the micro-structural constituent pearlite.
- (b) Raises the temperature at which the carbon change point occurs and hence the minimum temperature to which the steel must be heated before it can be hardened by quenching.

Plate I



FIG. 1. Pearlite (dark) and ferrite (light) in ordinary steel containing 0.3 per cent. carbon. $\times 100$.



FIG. 2. Laminated structure of pearlite. $\times 1,500$. Photograph taken from annealed stainless steel but also typical of pearlite in ordinary steel.



FIG. 3. Annealed stainless steel containing 0.15 per cent. carbon. $\times 100$.

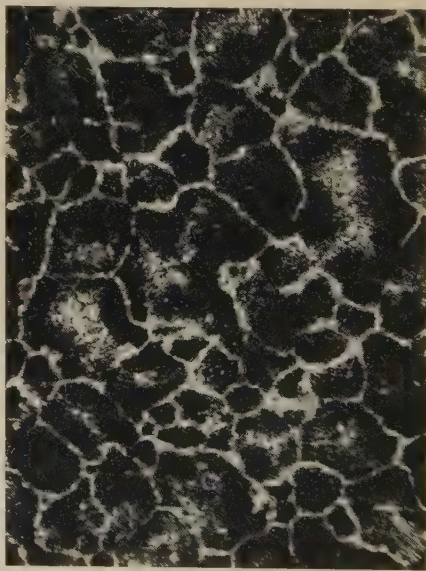


FIG. 4. Annealed stainless steel containing 0.5 per cent. carbon. $\times 300$.
(Note network of free carbide.)

- (c) Diminishes very markedly the speed at which carbon diffuses through the heated steel.
- (d) Induces in the steel the property of air hardening, that is, of hardening on air cooling from temperatures above the carbon change point.

The influence exerted by these changes is fundamental. The microstructures of ordinary carbon steels containing less than 0.9 per cent. carbon are known to consist of mixtures in varying proportion of two constituents, ferrite and pearlite. The former consists of practically pure iron, hence its name, while the latter is itself a mixture of iron and iron carbide, arranged alternately in the form of thin plates. These structural characteristics are now known to many users of steel but as a reminder and also as a standard with which to compare the structures found in stainless steels, they are typified in Figs. 1 and 2, the former representing the appearance of an ordinary mild steel containing 0.3 per cent. carbon when examined at a magnification of 100 diameters, and the latter, the fine plate-like structure of the pearlite, as seen at the highest powers of the microscope.

Experiment has shown that the iron and carbide of iron forming the pearlite are in such proportions that this constituent contains 0.9 per cent. carbon, hence it follows, because the ferrite contains no carbon, that in steels containing less than 0.9 per cent. carbon, the amount of pearlite increases proportionally to the carbon content from nil in carbon-free iron to 100 per cent. in steel with 0.9 per cent. carbon. Evidence of this is at hand in Fig. 1, in which the area occupied by the pearlite is approximately one-third of the whole. Increasing the carbon above 0.9 per cent., at which the whole mass consists of pearlite, leads to the formation of a third constituent, cementite or free carbide of iron, which may exist as a network round the grains of pearlite, similar to that shown in Fig. 4, as plates cutting across them or as more or less rounded particles.

From this summary of the structural characteristics of ordinary carbon steels and from the known properties of pure iron, a soft ductile metal, and of carbide of iron, a hard brittle compound, one can readily understand that the mechanical properties of steels containing up to 0.9 per cent. carbon are approximately a linear function of the carbon

content. Thus the tensile strength increases from about 18 tons per square inch in iron free from carbon to about 60 tons per square inch at 0.9 per cent. carbon, while at the same time the ductility, as represented by the elongation per cent. in a tensile test, gradually falls.

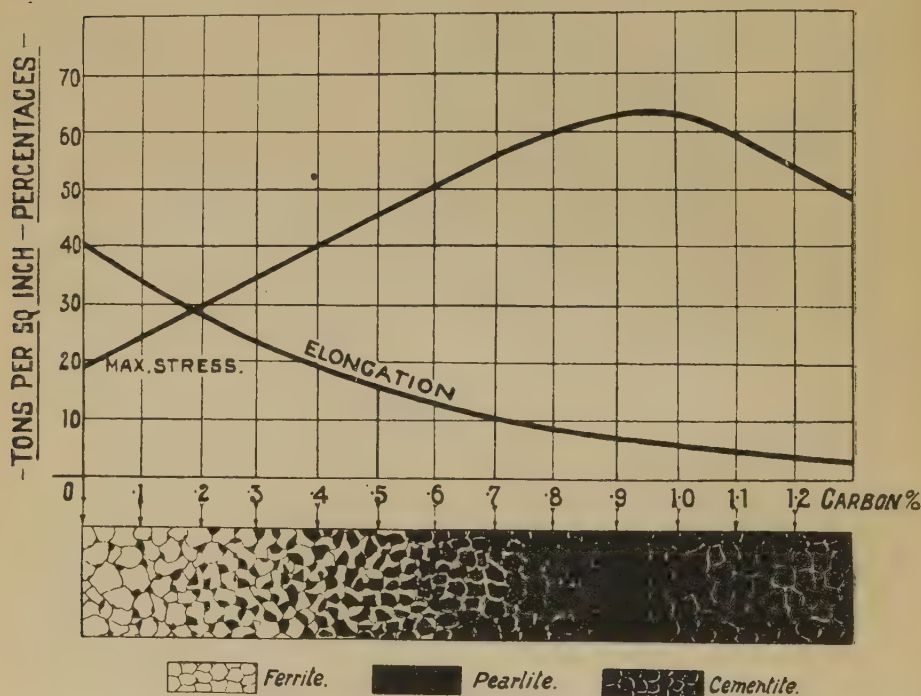


FIG. 5. Influence of carbon on the structure and mechanical properties of ordinary carbon steels.

With more than 0.9 per cent. carbon, the physical characteristics of the carbide of iron impress themselves in a more marked manner on the properties of the resulting steel. Up to this percentage of carbon, the carbide of iron has existed solely as part of the constituent pearlite, with the result that the lack of ductility of the carbide has been to a great extent masked because in pearlite each thin plate of carbide is sandwiched between two thicker plates of very ductile iron. The carbide existing free as cementite, however, is not subject to this mediating influence of ductile iron, hence it is not surprising to find that not only does the ductility continue to fall off as the carbon increases above

0.9 per cent., but in addition, the tensile strength begins to decrease as soon as the cementite is present in a sufficient amount to make its properties and structural condition felt. This brief analysis of the effect of increasing carbon content on the properties of ordinary steels is summarised in Fig. 5, which also shows diagrammatically the gradual change in structure with increasing content of carbon.

It will be apparent from the brief resumé given above that the factor which really governs the relation between the carbon content of steel and its mechanical properties is the amount of carbon contained in the constituent pearlite. If by any means, as for example the addition of alloys, the composition of this constituent is altered, then obviously the relation between the carbon content of the steel and its structure and properties will also be changed. In considering the influence on steel of any alloying metal, it is, therefore, of the greatest importance that its effect on the carbon content of pearlite should be known because it is this value which determines to a large extent the range of useful carbon content available in the particular alloy steel. Actually it is found that chromium has a very considerable influence on this carbon value.

In a paper published in 1920, the author* described some experiments for determining the composition of the pearlite in a series of chromium steels. In these experiments use was made of cemented bars of low carbon steel containing different amounts of chromium. The bars (which were one inch diameter and six inches long) were cemented for 24 to 36 hours at $1,000^{\circ}$ to $1,100^{\circ}$ C., so as to obtain a deep case; they were then slowly cooled after cementing, in order that the bars should be in the pearlitic condition. After cleaning with emery, the bars were turned down, over half their length, in cuts 0.25 millimetre thick and each cut analysed for carbon. From the remaining half of the bar, transverse sections were cut which were used for determining, microscopically, the depth to which free cementite existed in the bar. From the results obtained the relationship between the carbon content of the pearlite and the amount of chromium in the steel was plotted in a curve which is reproduced in Fig. 6. From this it will be seen that, in steel with 12 per cent. chromium, the pearlite contains

* "The Structure of Some Chromium Steels" *J.I.S.I.*, 1920, I, 493.

slightly more than 0.3 per cent. carbon instead of 0.9 per cent., as found in steels free from chromium. It will be evident, therefore, that carbon has a much greater effect in producing "steel" from iron with a high chromium content than from iron free from this alloying metal, and also that the useful range of carbon content of such high chromium material is likely to be much more restricted than in chromium-free steels. As an instance of this, it may be pointed out that,

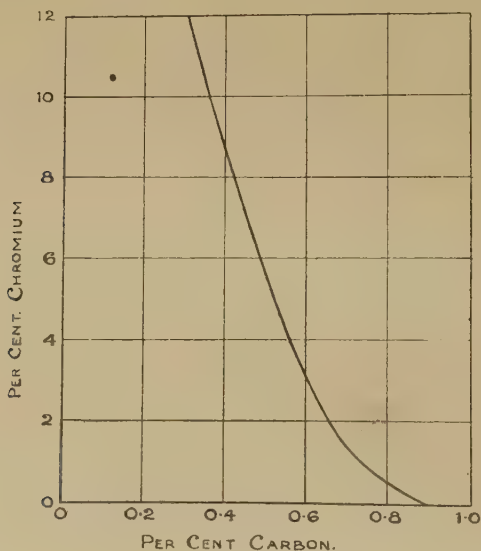


FIG. 6. Effect of chromium on the carbon content of pearlite.

from a structural point of view, annealed material containing 12 per cent. chromium and 0.5 per cent. carbon, contains a large amount of free carbide and corresponds in that respect to a tool steel containing 1.3 to 1.5 per cent. carbon.

This will be evident from a glance at Fig. 4 which shows the prominently visible network of free carbide existing in a steel containing 0.5 per cent. carbon and 12 per cent. chromium. In the same way, the grains of the pearlite in Fig. 3, representing a stainless steel containing 0.15 per cent. carbon, occupy almost half the area of the field and not about one-sixth of it as would be the case with an ordinary carbon steel containing this amount of carbon. The areas of pearlite in both these samples had a structure similar to

Fig. 2, when examined at very high magnifications. This typical photograph of pearlite was actually taken from a sample of stainless steel. All the photographs shown in Figs. 2 to 4 were taken from samples which had been very slowly cooled from a high temperature, such a treatment, as will be seen later, being necessary to obtain a pearlitic structure in high chromium steel.

It is necessary to emphasise this effect of chromium on the carbon content of pearlite. Experience of various types of ordinary steels during a considerable number of years has familiarised those dealing with steel with the carbon contents most suitable for specific purposes. Thus case-hardening steels contain, in general, 0.15 to 0.2 per cent. carbon, axles and mild steel forgings, 0.25 to 0.35 per cent., while in special forgings the percentage may rise to 0.40 or 0.45. Rails have a still higher carbon content, while railway and tramway tyres may contain up to 0.75 to 0.80 per cent. Tool steels contain still more carbon and to an amount varying with the purpose for which they are intended. Because this grading has been evolved in a more or less empirical manner from the observed properties of steel, it is perhaps not generally realised that it depends solely on the carbon content of the eutectoid pearlite. The fact is emphasised, however, in dealing with material such as stainless steel, the pearlite of which has a widely different carbon content. Owing to this marked difference, our ideas of the carbon content of steel most suitable for definite purposes, and evolved from usage with ordinary carbon steels, have to be completely modified in dealing with stainless steels.

As illustrated by the cementing experiments mentioned above, it is interesting to note the very high content of carbon which can be introduced into steels containing large amounts of chromium. It is well known that in ordinary chromium-free iron there is very great difficulty in introducing more than about 1.8 per cent. carbon even by prolonged cementation. In the experiments mentioned above, the steels with a chromium content in the range used for stainless material were cemented for 36 hours at about 1,100° C.; the outer layers of the bars thus treated contained approximately 3.0 per cent. carbon, while penetration had taken place to a depth of about three-eighths of an

inch. These highly-carburised layers contained, of course, very large quantities of free carbide.

Changes in Structure Occurring on Heating and Cooling. Passing on to consider the further effects of chromium as set out in paragraphs (b), (c), and (d), page 20, all of which have a considerable bearing on the heat treatment of steel, it may be advantageous to recall briefly the effect of heat treatment on the structure and properties of ordinary carbon steels.

If a sample of ordinary mild steel, containing about 0.3 per cent. carbon, is gradually heated, no appreciable change is produced in its structure until a temperature of about 740°C. is reached. Similarly, quenching samples of the steel from any temperature below this value produces no appreciable change in the properties of the material. At about 740°C. , the carbon change point generally referred to as Ac.1 occurs, being accompanied, as is well known, by a marked absorption of heat. During this change, the pearlite in the steel changes from a mixture of two separate materials, iron and carbide of iron, into a homogeneous solid solution which, for convenience, is called austenite. If a small sample of the mild steel be rapidly quenched in water immediately after this change has taken place, it will be found that the original structure of ferrite and pearlite has been replaced by another having the same general pattern as before but in which the pearlite areas are now occupied by a substance which shows no signs of the duplex structure of the pearlite. This new constituent is called martensite and to it is due the hardness of quenched steel.

If the heating of the mild steel is continued, the solid solution, austenite, gradually dissolves the surrounding ferrite as the temperature rises until, finally, the whole mass consists of austenite. If small samples be rapidly quenched from a series of gradually increasing temperatures above 740°C. , it will be found that the amount of the constituent martensite in these quenched samples gradually increases while that of the ferrite gradually gets less until, finally, the whole mass consists of martensite.

In the same way, if ordinary steel containing more than 0.9 per cent. carbon be heated, a similar series of changes takes place; the pearlite is first replaced, at the Ac.1 change,

by austenite which then, as the temperature rises, gradually dissolves the cementite.

Although martensite does not possess the duplex structure of pearlite it shows, on more or less deep etching, a characteristic structural appearance which suggests a series of interlacing needles. This appearance, which is illustrated in Fig. 11, is connected with the crystalline structure of the martensite or the austenite from which it was formed. The size and distinctness of this structural pattern increases markedly as the temperature of quenching is raised above that of the A_{c1} point.

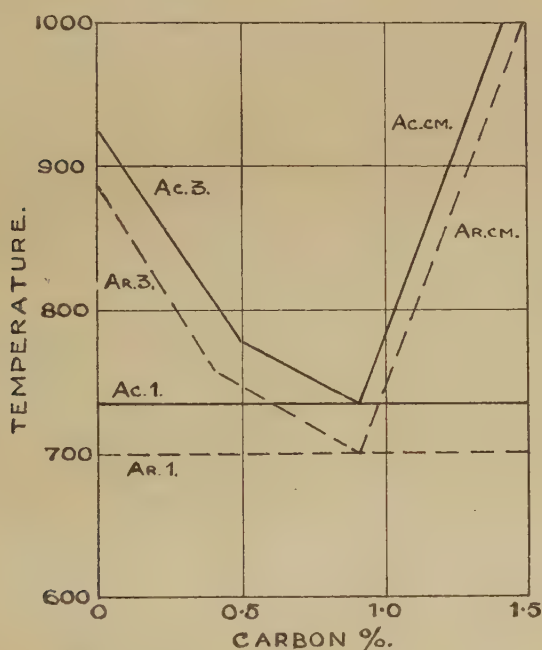


FIG. 7. Effect of carbon content on the critical changes occurring on heating and cooling ordinary steels.

It would be expected that the temperature required to produce, on heating, a homogeneous mass of austenite in any particular steel, will vary with the amount of ferrite or cementite which it contains; this is actually the case and the results of numerous experiments in this direction are summarised in the diagram shown in Fig. 7. This shows, again as would be expected, because it affects only the

constituent pearlite common to all steels, that the carbon change point, on heating, occurs at sensibly the same temperature with all steels, a fact indicated by the continuous line, *Ac.1** running across the diagram at 740°C . The temperature of final solution of the ferrite is marked by the line *Ac.3*, which falls from about 920°C ., with vanishing carbon content to 740°C . at 0.9 per cent., where it joins the *Ac.1* line. In the same way, the line *Ac.cm.* represents the temperature of complete solution of the cementite and this will be observed to rise very rapidly as the amount of carbon increases above 0.9 per cent.

On slowly cooling the steels, the corresponding changes take place in the reverse order, but at temperatures approximately 50°C . below those at which they occurred on heating. Thus the dotted lines *Ar.3* and *Ar.cm.* mark the beginning of the separation of ferrite and of cementite respectively while *Ar.1* similarly marks the change of austenite back into pearlite.

From what has been said it will be evident that, of all carbon steels, the simplest, from the point of view of changes occurring during heat treatment, is one containing 0.9 per cent. carbon. Such a steel normally consists solely of pearlite; on heating it has one change point, at 740°C ., at which the pearlite changes to austenite. A small sample rapidly quenched from any temperature above this consists entirely of martensite. A steel of this composition is frequently called "eutectoid," a term which has been coined, from Greek words, to indicate that the change points which occur in it, on heating, are completed at a lower temperature than with steel of any other carbon content. This, of course, is evident from the diagram Fig. 7. Steels which contain less carbon than 0.9 per cent. are termed hypoeutectoid, and those with higher carbon, hypereutectoid.

If any confidence may be placed in analogy it would be expected that in stainless steels, the simplest changes on heating and cooling will be found also in steel of eutectoid composition and actually it is found that the changes in

* The use of the "shorthand sign" *Ac.1* is readily understood when it is remembered that these letters are an abbreviation for the French words *arrêt* (arrest), *chauffage* (heating). The numeral 1 distinguishes this point from others which occur at other temperatures on heating. Similarly changes on cooling are indicated by the letters *Ar*, the second letter indicating *refroidissement* (cooling).

Plate II

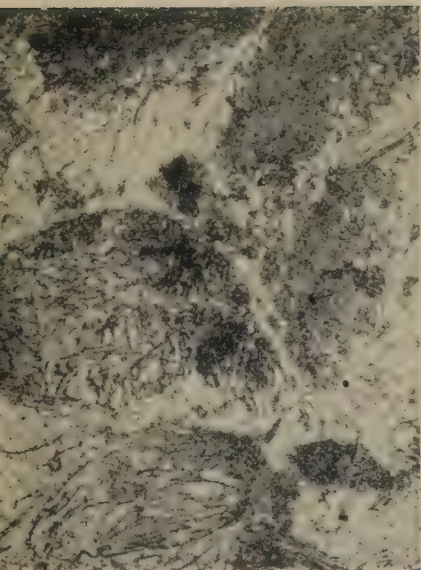


FIG. 8. Slowly cooled from a high temperature producing a pearlitic structure.

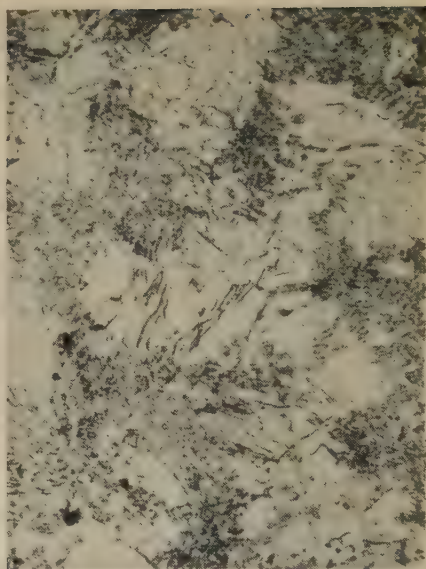


FIG. 9. Sample similar to Fig. 8 reheated to 825°C. and quenched in water.

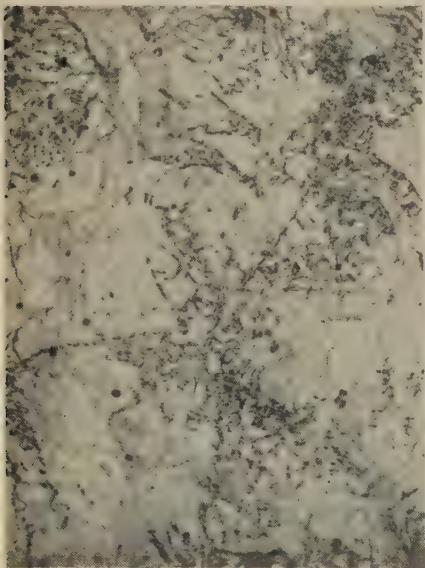


FIG. 10. As Fig. 9, but reheated to and quenched from 950°C.



FIG. 11. As Fig. 9, but reheated to and quenched from 1050°C.

FIGS. 8, 9, 10, 11. STAINLESS STEEL CONTAINING 0.3 PER CENT. CARBON AND 12 PER CENT. CHROMIUM AFTER VARIOUS TREATMENTS.

All magnified 750 diameters.

To face page 29.]

structure and properties occurring in stainless steels are much more readily understandable if attention is first given to steel of such composition.

One of the effects of the presence of large amounts of chromium in steel, as noted on page 21, is the steel acquires the property of air hardening, that is, of hardening on cooling in the air from temperatures above the carbon change point in the same way that ordinary carbon steel hardens by quenching in water from these temperatures. Owing to this property, to which more detailed consideration will be given later, it is necessary to cool stainless steel very slowly from a fairly high temperature in order to produce in it a pearlitic structure. A steel, however, containing about 12 per cent. chromium and 0.30 per cent. carbon, i.e., of eutectoid composition, slowly cooled from a temperature of 1,000° C. or over consists of well-defined pearlite, as shown in Figs. 2 and 8, and has a Brinell number of about 200. If small samples of such a steel are quenched from a series of gradually increasing temperatures it will be found that no change in the structure or the hardness of the quenched piece is produced until a temperature of about 800° C. is reached, owing to the fact, stated in paragraph (b), page 20, that chromium raises the temperature at which the carbon change point occurs. Here the Ac.1 change occurs and, as in ordinary steels, is accompanied by a well-defined absorption of heat. Whereas, however, in ordinary carbon steels the solution of the carbide in the pearlite takes place very rapidly at the Ac.1 point, in stainless steels, as in all high chromium steels, it takes place much more slowly. As a result of this, the absorption of heat in such steels, which is generally referred to as Ac.1, is actually only the commencement of this change because only part of the eutectoid carbide dissolves at that temperature, the remainder going progressively into solution as the temperature rises over a range of 150° to 200° C. above this point. For convenience, however, the temperature marking the heat absorption at the beginning of this range will be referred to in the following pages as the Ac.1 change. If two small samples of the steel in question are quenched, one immediately below and the other immediately above this Ac.1 point, it will be found that this is considerably harder than that and, when prepared as a microsection, etches more slowly, but the microstructures

of the two appear to be almost identical. In that quenched below the change point, the structure consists of pearlite, or fine lamellae of carbide more or less evenly distributed through a ground mass of ferrite being, in fact, precisely similar to Fig. 8; that quenched above the change consists of lamellae of carbide, less in number than before but similarly distributed in a background of martensite. Owing, however, to the lamellae of carbide being closely packed, the background has little chance to develop any distinctive signs of martensitic structure. The similarity between the structures of two such samples as these is illustrated by comparing Figs. 8 and 9, the latter representing a sample quenched from 825°C. , i.e., about 25° or so above Ac.1 . The resemblance between the two structures is evident as is also the large amount of carbide remaining undissolved in the sample quenched from 825°C.^*

As the temperature rises above the Ac.1 point, the amount of carbide remaining undissolved becomes less and less, while in samples quenched from a series of gradually increasing temperatures, the appearance of martensite becomes more pronounced. Finally, at a temperature of about $1,000^{\circ}\text{C.}$, depending to some extent on the rate of heating, the time of soaking at the maximum temperature and also on the chromium content, complete solution of the carbide is obtained and samples quenched, or air cooled, from this temperature or above consist of martensite—see Figs. 10 and 11.

As a consequence of the gradual solution of the carbide above the Ac.1 change point, stainless steel does not attain its full hardness on quenching immediately above this point; on the contrary, the hardness of quenched samples increases as the quenching temperature is raised through the range of 150° to 200°C. above this point during which,

* Probably the most convenient etching reagent for these steels is a 10 per cent. solution of hydrochloric acid in alcohol; the time of etching with this reagent varies according to the condition of the steel, being approximately three to five minutes for annealed samples and twenty to thirty minutes for those which have been hardened.

In order to show the carbide in stainless steels, the reagent proposed by Murakami is also very useful. This reagent (an aqueous solution containing 10 per cent. of caustic potash and 10 per cent. of potassium ferricyanide) darkens the carbides, leaving the other constituents unaffected and has, therefore, an action similar to that of sodium picrate on ordinary steel. It may be used cold, in which case about 10 or 20 minutes' attack may be required, or boiling, when the attack is more rapid.

as previously described, the carbide is gradually dissolving. This is shown in Fig. 12, which represents the Brinell hardness numbers obtained from a series of samples quenched at gradually increasing temperatures.

Having traced the changes occurring on heating a sample of stainless steel to the point at which it becomes fully hardened when quenched, the structure so produced consisting entirely of martensite, attention may next be given to the effect produced by tempering such a sample. If a fully hardened sample of ordinary carbon steel of eutectoid composition be reheated to a series of gradually increasing temperatures, it is well known that the hardness of the steel is gradually reduced.

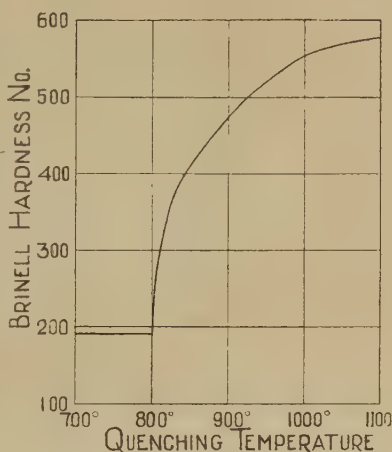


FIG. 12. Brinell hardness numbers obtained from annealed stainless steel (0.30 per cent. carbon) after water quenching from the temperatures indicated.

After tempering up to about 200° C., there is practically no loss of hardness but as the temperature rises above this figure up to 740° C., the Ac.1 point, the hardness falls almost uniformly. This is indicated in curve B in Fig. 13, which shows the Brinell hardness numbers obtained on tempering such a steel at a series of gradually increasing temperatures. From each tempering heat the sample was quenched in water, hence the Ac.1 point which occurred at 740° C. is marked by a sudden increase in the hardness. On tempering in the same manner a hardened sample of stainless steel, changes are produced similar to those occurring in the ordinary carbon steel except that they occur at much higher temperatures. With the high chromium steel, the hardness remains almost unchanged up to 500° C. or slightly higher. At about 550° C. tempering takes place rather suddenly, the hardness falling rapidly so that by the time the temperature has reached 600° C. the Brinell hardness number has a value of 250 to 300. From 600° C. up to 750° or 800° C., the hardness falls slowly and steadily to a value of about

200 Brinell. In curve A, Fig. 13, are plotted the Brinell hardness numbers obtained on tempering such a steel at gradually increasing temperatures and a comparison of this with curve B in the same diagram indicates clearly the differences between the two types of steel. Curve A also shows very plainly the three ranges of tempering temperature, mentioned above, which occur in the tempering of stainless

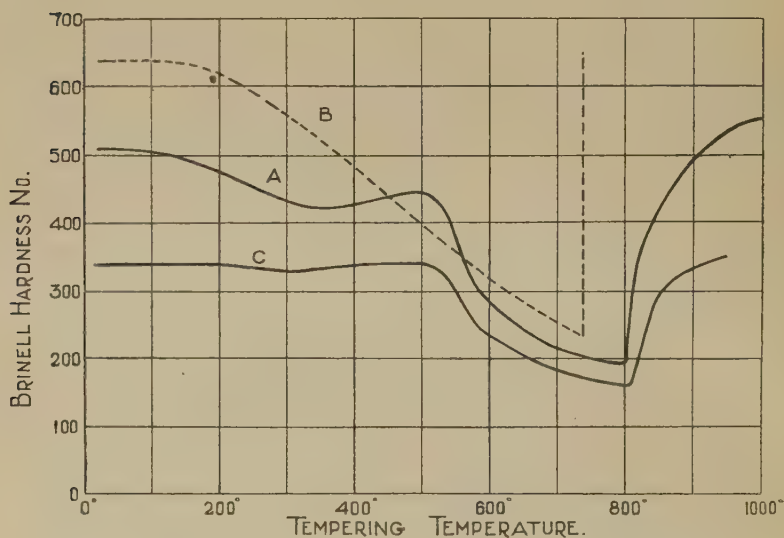


FIG. 13. Brinell hardness numbers obtained on tempering hardened steels at gradually increasing temperatures, the samples being water quenched from each tempering heat.

- A. Stainless Steel. (0.30% Carbon).
- B. Carbon Steel (0.90% Carbon).
- C. Stainless Iron (0.07% Carbon).

steel. From a practical point of view, the third range, from about 600° to 750° or 800° C. is very interesting and useful, because a steel which on tempering does not alter very much in hardness or tensile strength over a range of fifty or a hundred degrees of tempering temperature is obviously more easy to heat treat on a practical scale than one in which the hardness changes rapidly as the temperature increases. On the other hand, the very sudden fall in hardness occurring between 500° and 600° C. makes it difficult to secure prescribed properties by tempering stainless steel in this range.

Plate III

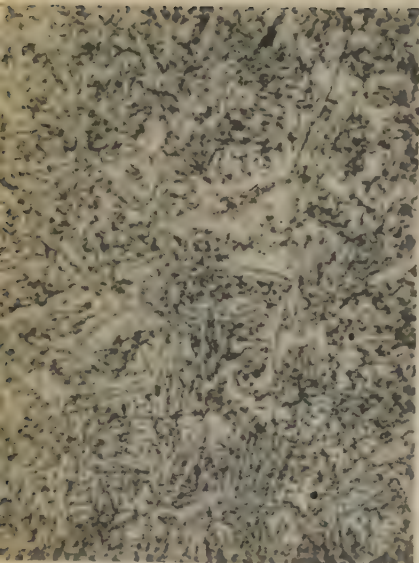


FIG. 14. Hardened and then tempered at 700°C. Brinell 207. $\times 1,000$.

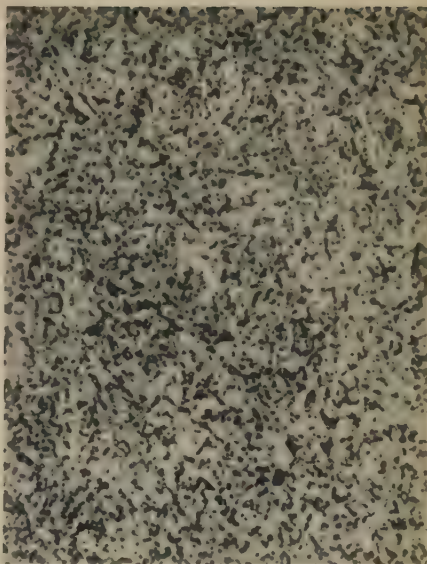


FIG. 15. Oil hardened 900°C. Brinell 437. $\times 1,000$.

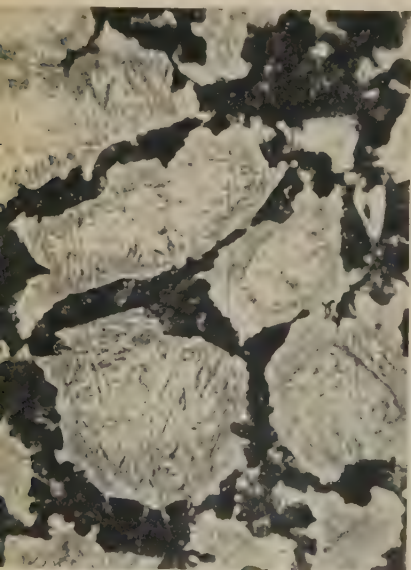


FIG. 16. Martensite (light) and troostite (dark) in sample moderately slowly cooled from 200°C. Brinell 364. $\times 250$.



FIG. 17. Annealed 860°C. Brinell 170. $\times 1,000$.

FIGS. 14, 15, 16, 17. STAINLESS STEEL. 0.30 PER CENT. CARBON.

To face page 33.]

The alterations in hardness occurring on tempering the hardened sample of stainless steel are accompanied by changes in the structure of the steel. After tempering at temperatures up to 500°C. , in the range in which the hardness remains practically constant, the structure still consists of martensite similar to that in the untempered sample though it probably requires a shorter attack than the latter by the etching fluid to develop its structure. The sudden drop in hardness occurring between 500° and 600°C. is accompanied by a change in the structure, the martensite being replaced by sorbite consisting of very fine particles of carbide, only visible at the highest powers of the microscope, embedded in a ground mass of ferrite. In the third range of tempering, between 600° and 750° or 800°C. , the particles of carbide, which have separated out previously, gradually coalesce into larger globules. Such a fully tempered sample has therefore the structure shown in Fig. 14.

If the heating of the hardened and tempered sample is continued to still higher temperatures, the same sequence of events as was described on page 30, takes place again. The Ac.1 point occurs at about 800°C. , austenite is again formed, part of the carbide goes into solution while the remainder gradually dissolves as the temperature rises above this point. Similarly the hardness of quenched samples increases with increase in quenching temperature as indicated in the right hand part of curve A in Fig. 13. The structure of such a sample quenched at 900°C. is shown in Fig. 15, and this may be regarded as typical of the structure of normally hardened stainless steel.

Effect of Rate of Cooling on Hardness and Micro-structure. Several references have already been made to the effect of comparatively large amounts of chromium in inducing in steel the property of air hardening. It may be advantageous to consider this in a little more detail. It is a matter of general knowledge that if a piece of ordinary carbon tool steel is rapidly quenched in water from a suitable temperature, it is hardened. If quenched from the same temperature in oil, or other medium giving a slower rate of cooling than water, it is less hard while if cooled at the still slower rate obtained by allowing a small sample to cool freely in the air, it is much softer. These results suggest that there is a distinct connection between the rate of

cooling of a sample and the degree of hardness produced in it, and also that in order to harden ordinary carbon steel a very rapid rate of cooling is necessary. That this is the case is familiar to the smith, who knows that if he quenches in water, from a good hardening temperature, a piece of carbon tool steel in the form of a bar about half an inch in diameter, it will be hardened throughout and will break with a fine even fracture. If, however, he similarly quenches from the same temperature a larger sized bar, e.g. one and a half inches in diameter, of the same steel, this will not harden to the centre but in breaking will show a soft core.

If the hardening experiment, using the different rates of cooling given by water, oil and air quenching, be repeated with a steel containing the same amount of carbon as before and in addition 1.5 or 2.0 per cent. of chromium, it will be found that both the bar quenched in oil and that quenched in water are as hard as the water-quenched bar of ordinary carbon steel. On the other hand, the bar cooled in air is still much softer than either of these. This suggests that the presence of the chromium has allowed the steel to harden at a slower rate of cooling. Chromium actually has this action and to an extent which increases with the amount of this element present, so that with such a high percentage of chromium as is contained in stainless steel, the changes which should occur on cooling the steel from a hardening heat are retarded to such an extent that the steel hardens when air-cooled from such a temperature. The hardness so produced in stainless steels, however, is not independent of the rate of cooling; variations in this rate effect similar changes to those produced by different rates of cooling in ordinary steels, but the actual values of the rates necessary to give similar effects in the two types of steel are widely different. As with ordinary steel, so with stainless steel, there is a fairly definite rate of cooling which must be exceeded to bring about hardening. This rate, however, varies with the composition of the steel and also, in any given steel, with the temperature from which it is cooled. The higher this temperature is above the A_{c1} point, the slower the rate at which the steel may be cooled and yet be hardened. This is illustrated in Fig. 18, which represents the Brinell hardness numbers obtained from samples of a stainless steel, of approximately eutectoid composition, after being cooled

at different rates from 860° and $1,200^{\circ}\text{C.}$, respectively, the rate of cooling being measured by the time taken to cool over the range 850° to 550°C.^* The curves in this diagram show that, to obtain a Brinell hardness number of at least 400 in the steel tested, the cooling time should not exceed about two minutes when cooled from 860°C. , but may

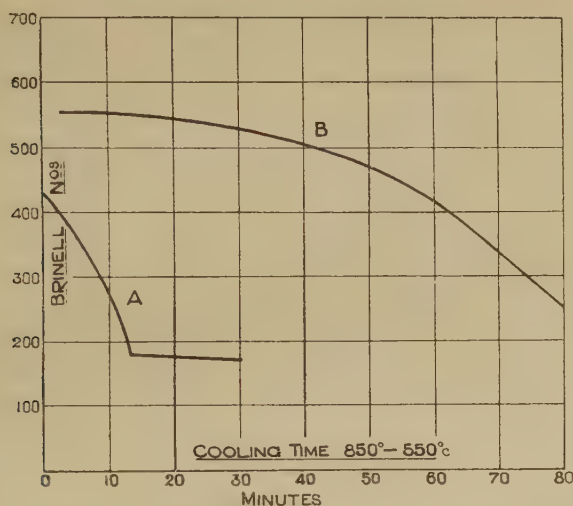


FIG. 18. Effect of varying rates of cooling on the Brinell hardness number of stainless steel when cooled from 860°C. (curve A) and $1,200^{\circ}\text{C.}$ (curve B).

reach 60 minutes when the maximum temperature is $1,200^{\circ}\text{C.}$ With slower rates of cooling than these, the steel becomes progressively softer until the completely annealed condition is obtained, in which state the steel corresponds to the normalised condition of ordinary carbon steels. The actual rates of cooling necessary to harden or to anneal any particular steel depend on its carbon and chromium content, and are also materially affected by the content of other elements present, notably nickel. The rate at which a steel must be

* The range 850° to 550°C. was adopted for taking the cooling rates in these experiments largely from the point of view of convenience. Actually, however, it is found by experiment that this interval of temperature includes practically all the range in which the *A_r1* point in stainless steel takes place on slow cooling, and that providing this range of temperature is passed through at the requisite rate, the speed of cooling below 550°C. , or in any case 500°C. , does not materially affect the hardness produced. To give some concrete idea of the meaning of the rates of cooling given in Figure 18 it should be mentioned that a bar three-quarters of an inch in diameter on cooling freely in the air occupies about $1\frac{1}{2}$ minutes in passing through the range 850° to 550°C. , providing no evolution of heat occurs in the sample itself.

cooled in order to anneal it completely is slower the higher the chromium and nickel content ; on the other hand, high carbon alloys are more easily annealed than those of lower carbon, but otherwise of similar composition, i.e., they anneal at faster rates of cooling.

The actual microstructure obtained on annealing stainless steel also depends on the maximum temperature to which the steel was heated prior to the slow cooling. If this temperature was sufficiently high to dissolve all the carbide, a pearlitic structure, practically indistinguishable from that of ordinary carbon steels and similar to Figs. 2 and 8, is obtained on complete annealing. For the production of such a structure a very slow rate of cooling is necessary as will be evident from Fig. 18. With rates of cooling, from this temperature, intermediate between this and that necessary to harden the sample (that is, rates of cooling such as would give Brinell hardness numbers between 400 and 200, see Fig. 18), the structure consists of mixtures of martensite and finer or coarser forms of pearlite. The sequence of structural changes obtained in this range of cooling rates may best be illustrated by considering a rate of cooling just sufficient to harden the sample completely. As the cooling rate becomes gradually slower than this, the structure which, in the fully hardened sample, consisted entirely of martensite, now begins to show small areas which etch very rapidly and appear under the microscope as black structureless masses. These areas are known as troostite, they consist of a mixture of iron and carbide of iron, similar to pearlite, but in which the separate particles are so small as to be indistinguishable separately at the highest powers of the microscope. As the rate of cooling becomes still slower, the amount of troostite increases, the hardness correspondingly decreasing, until the whole mass consists of this constituent, and then with still slower rates the particles of carbide and of iron in the troostite get coarser and coarser till, finally, well-developed laminated pearlite is obtained. The progression of structure from martensite to pearlite is therefore precisely similar to that obtained on varying the cooling rates for ordinary carbon steel, except that the rates for producing similar structures in the two steels are widely different. Fig. 16 shows a structure consisting of martensite and troostite ; the sample

Plate IV

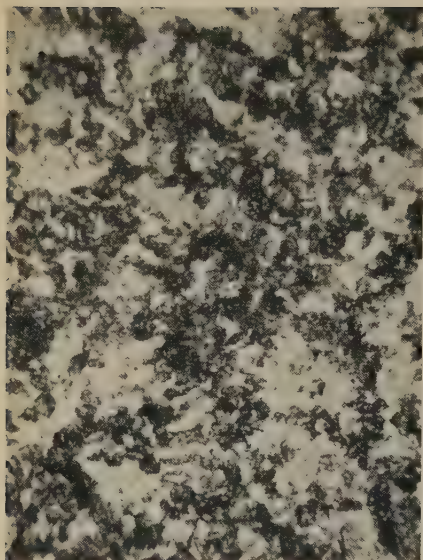


FIG. 19. Stainless steel cooled from 860°C. at a rate not quite fast enough to harden it. (Brinell 245.) Etched with picric acid. $\times 250$.

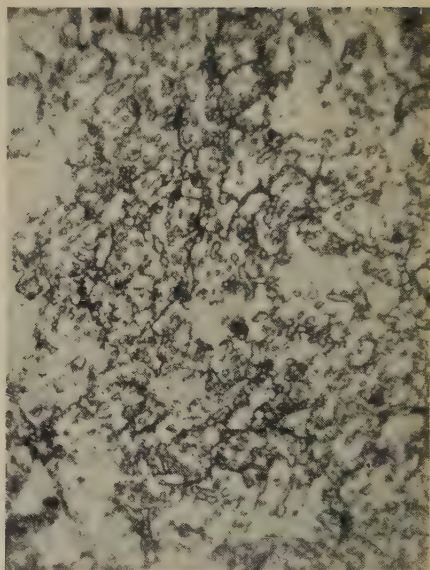


FIG. 20. Dark parts of Fig. 19. $\times 1,500$.

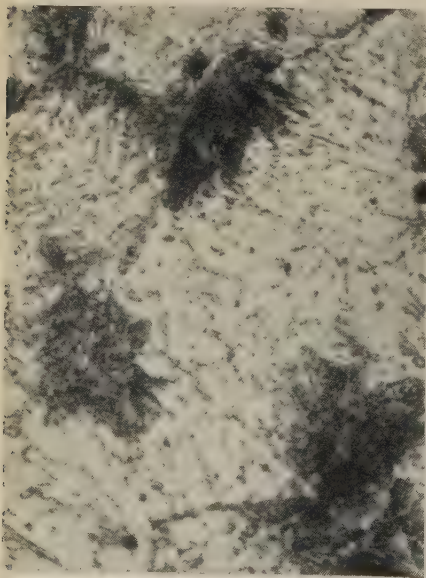


FIG. 21. Stainless steel with 0.15 per cent. carbon, slowly cooled from 1,050°C. $\times 750$.

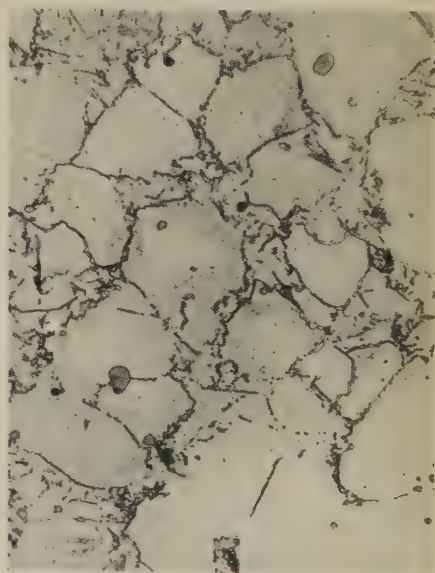


FIG. 22. Stainless iron with 0.07 per cent. carbon, slowly cooled from 1,050°C. $\times 750$.

from which this was taken had a Brinell hardness number of 364.

If, however, the steel is cooled more or less slowly from temperatures insufficiently high to dissolve all the carbide, the microstructures obtained differ from those described in the last paragraph. It has been shown on page 30 that when stainless steel is quenched from this range of temperature, the structure consists of particles of carbide distributed in a ground mass of martensite (see Figs. 9, 10, and 15). With somewhat slower rates of cooling than that necessary to harden the steel from this range of temperature (that is, corresponding to about 5 to 12 minutes, curve A, Fig. 18), the background etches darker and the structure looks confused but no real appearance of troostite, such as is obtained on cooling from high temperatures, is produced. Finally, with still slower rates of cooling one obtains a completely annealed material having a granular structure, such as is shown in Fig. 17, which is very similar to that produced by hardening and fully tempering the steel except that the grains of carbide are considerably larger in the annealed sample than in the other; this will be evident on comparing Figs. 14 and 17.

It is possible, however, to obtain with these semi-annealed samples some interesting etching figures with the five per cent. solution of picric acid in alcohol which is generally used for the microscopical etching of samples of ordinary steel. This reagent has practically no effect on sections of stainless steel which have been hardened or hardened and tempered. If, however, samples cooled at the intermediate rates described in the last paragraph are etched with picric acid an appearance of troostite is produced. Thus Fig. 19 shows at a medium magnification a sample cooled from 860° C. at a rate of 9 minutes and having a Brinell hardness number of 245, after etching with picric acid; the appearance strongly suggests a mixture of martensite and troostite. If, however, such samples are examined under the highest powers of the microscope it will be seen that the patches are not troostite but groups of carbide granules, as shown in Fig. 20. A probable explanation of the appearance shown in Fig. 19 is that the darker parts of the section are more readily attacked than the rest by the weak picric acid because

they are the initial decomposition centres of the martensite.

If samples slowly cooled from high temperatures, and consisting of mixtures of martensite and troostite (e.g., similar to Fig. 16) are etched with picric acid, the troostite is distinctly etched while the martensite remains quite unattacked. If such a sample be subsequently tempered at about 700° (so as to give in the martensite areas a structure similar to Fig. 14) and then etched with picric acid, again only the troostite areas are etched. The areas having the hardened and tempered structure, which were formed from the martensite existing before tempering, remain quite white. These results with picric acid etching have an interesting bearing on the relative resistance to corrosion of annealed and hardened and tempered samples of the steel; they will be referred to later.

Influence of Carbon Content on Micro-structure.

Having discussed the changes occurring in a stainless steel of approximately eutectoid composition, the influence of varying carbon content may next be considered.

When annealed at high temperatures, $1,000^{\circ}\text{C.}$ and upwards, steels with lower carbon content than eutectoid composition, consist of mixtures of ferrite and pearlite similar to those of ordinary mild steels except that there is a distinct tendency for the ferrite in the high chromium steels to contain isolated globules and laminae of carbide. This is illustrated in Fig. 21, which represents the structure of a steel with 0.15 per cent. carbon slowly cooled from $1,050^{\circ}\text{C.}$ The carbide particles can also be seen in Fig. 3, which shows the same steel at a lower magnification. It will be noted that the pearlite areas in this sample occupy about half the field, as would be expected, because the carbon content of the steel is about half that of the pearlite in stainless steel. When the carbon is reduced to the limits generally found in stainless iron, 0.10 per cent. or less, the carbide in the pearlite tends to ball up so that such low carbon material when annealed from high temperatures often consists of ferrite grains with globules of carbide tending to form a network round them. A typical example is shown in Fig. 22. On the other hand, when such hypoeutectoid steels are air-cooled or quenched in water or oil from high temperatures, they consist entirely of

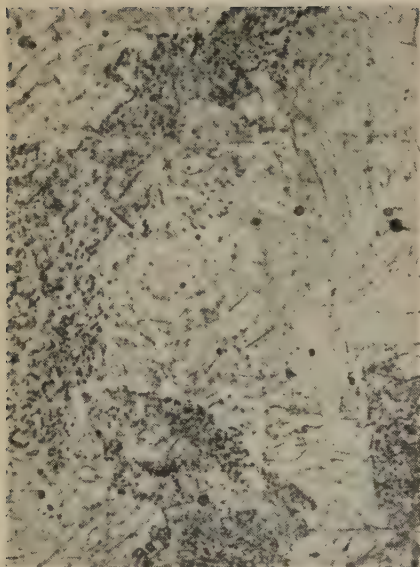


FIG. 23. Material shown in Fig. 21 after reheating to 900°C. for one hour and then quenching—showing carbide remaining undissolved. $\times 1,000$.

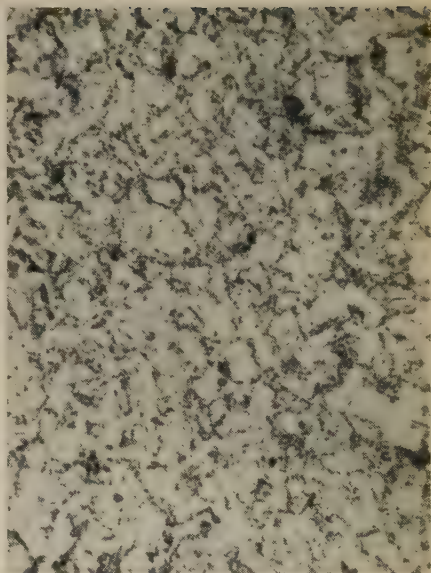


FIG. 24. Stainless iron, 0.07 per cent. carbon, 13.3 per cent. chromium, hardened 950°C. and tempered 700°C. (Brinell 174). $\times 1,000$.



FIG. 25. Stainless iron, 0.07 per cent. carbon, 13.3 per cent. chromium, water quenched from 850°C. (Brinell 238). $\times 300$.

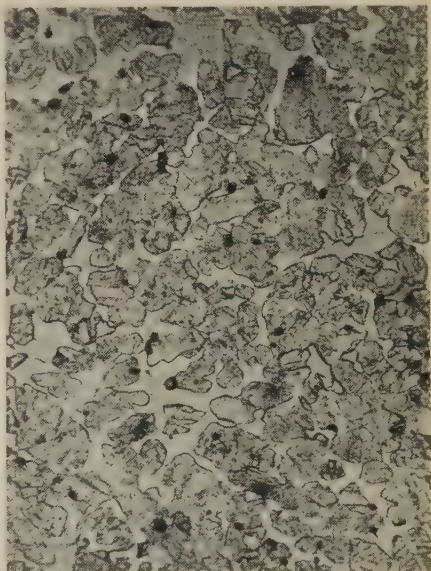


FIG. 26. Same steel as Fig. 25 but quenched from 900°C. (Brinell 281). $\times 300$.

martensite unless the carbon is very low, when free ferrite may also be present, more particularly in air-cooled samples. The presence or absence of ferrite is also materially influenced by the composition of the steel apart from chromium and carbon; thus low carbon material containing comparatively large amounts of silicon is more likely to contain ferrite than a steel low in silicon but otherwise similar in analysis, when both are treated in the same way.

On tempering hardened samples of the low carbon alloys, the Brinell hardness number falls in a manner similar to that of the higher carbon steel, as shown in curve C, Fig. 13. On passing the carbon change point, the carbide in the pearlite also behaves in the same way as that in eutectoid steel; that is, part of it dissolves at the actual absorption of heat and the remainder as the temperature rises above this. The temperature required for complete solution of the carbide under ordinary conditions of heating, e.g., soaking for 30 to 60 minutes at the maximum temperature, depends to some extent on the previous distribution of the carbide; if the latter be evenly distributed, as occurs when a previously fully hardened sample, consisting entirely of martensite, is reheated, complete solution is obtained somewhat earlier than if the same steel had been previously annealed so as to give a structure of ferrite and pearlite. This difference is understandable from the very slow rate of diffusion of the carbon in such high chromium steel, and the greater distance which the carbide has to diffuse in the case of the sample with the ferrite and pearlite structure. The persistence of the carbide particles may be illustrated by Fig. 23, which is taken from a small disc, six mm. thick, of steel, having initially the structure shown in Fig. 21, after reheating for one hour at 900° C., followed by quenching in water. Even in extremely mild steels, with 0.10 per cent. carbon or less, carbide may be detected in samples quenched 50° to 100° C. above the carbon change point.

The Ac.3 line for these steels, representing the temperature of the complete solution of the free ferrite on heating, has not yet been worked out; its position appears to alter quite considerably with variations in the content of silicon, manganese and nickel, small but variable amounts of which are almost always found in stainless material. The ferrite, however, is gradually dissolved as the temperature

risers above the Ac.1 point. Figs. 25 and 26 show the structure of small samples of steel containing 0.07 per cent. carbon and 13.3 per cent. chromium after quenching from 850° and 900° C., respectively, and illustrate the gradual solution of the ferrite. When quenched from still higher temperatures, the structure became entirely martensitic.

After hardening and then tempering between 600° and 750° C., low carbon alloys consist of ferrite with particles of carbide more or less evenly distributed—see Fig. 24. When annealed from temperatures just above the Ac.1 point, they consist of ferrite and rather coarse granules of carbide, similar to those in Fig. 17, but less in number, the distribution of the granules depending to some extent on the previous history of the sample.

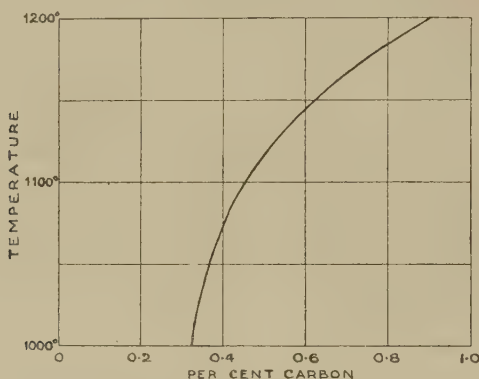


FIG 27. Solubility of free carbide in stainless steel (11.2 per cent. chromium) at high temperatures.

Stainless steels of hypereutectoid composition behave in a manner analogous to ordinary high carbon steels. The excess carbide gradually dissolves after the eutectoid carbide has been taken into solution. In the paper previously referred to,* the author traced out the solubility line of the free carbide in a steel containing 11.2 per cent. chromium; the results obtained are reproduced in Fig. 27, from which it will be seen that in such a steel, the carbide corresponding to 0.35 per cent. carbon, is dissolved at 1,000° C., to 0.45 per cent. at 1,100° C. and to 0.9 per cent. at 1,200° C. As with

* *J.I.S.I.*, 1920, I, p. 493.

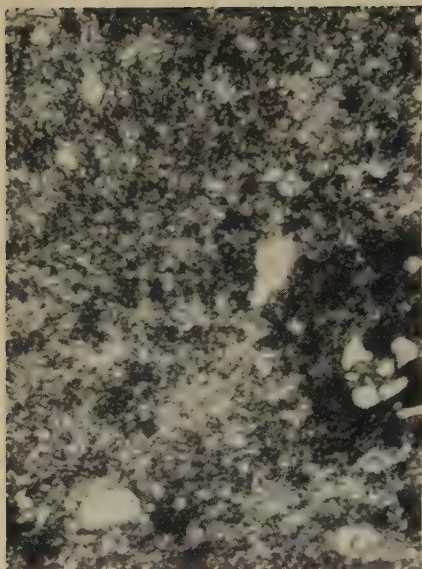


FIG. 28. Steel containing 1.01 per cent carbon and 11.8 per cent. chromium, hardened and fully tempered (Brinell 241). $\times 1,000$. (see page 45).

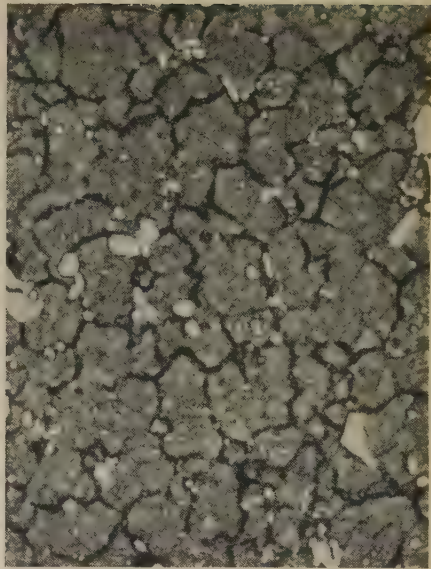


FIG. 29. Same steel as Fig. 28 but quenched from 1,000°C. (Brinell 627). $\times 750$. (see page 45).



FIG. 30. Austenite obtained by quenching, from 1,200°C., steel with 0.67 per cent. carbon, and 14.1 per cent. chromium. $\times 500$. (see page 45).

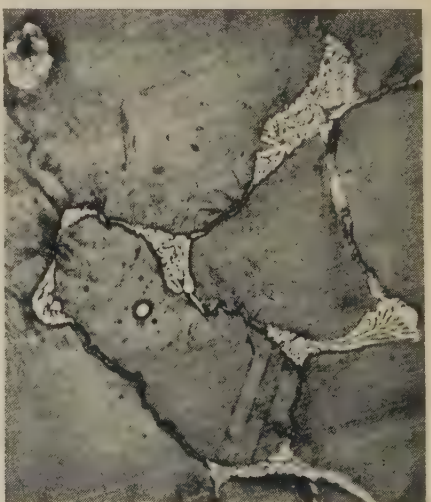


FIG. 31. Burnt sample of high carbon stainless steel showing characteristic eutectic structure. $\times 500$.

the solution of the eutectoid carbide, there is probably a considerable "time element" in the solubility of the excess carbide. The figures given refer to experiments in which the samples were held at the indicated temperature for half-an-hour. With considerably longer periods of soaking, the amounts of carbon dissolved at any temperature would probably be somewhat greater.

Stainless Steels with High Carbon Content. Steels which have a relatively high carbon content, e.g., 0.8 to 1.0 per cent., can perhaps hardly be referred to as ordinary types of stainless steel because, as will be seen later, their resistance to corrosion is considerably less than that of steel with lower carbon content but otherwise similar in analysis. They are, however, of considerable interest theoretically and as their properties show in a somewhat exaggerated form the effects, not always advantageous, of using a higher carbon content than is normally present in stainless steel, it may not be out of place to consider them briefly. Such steels contain very large amounts of free carbide and as this is only completely taken into solution at very high temperatures, if at all, their heat treatment, especially as regards refining a coarse structure, presents obvious difficulties. Owing to the presence of this large amount of carbide, they are not particularly soft even when fully tempered. Such high carbon steels are also very easily burnt; however, the characteristic structure of such burnt steel, showing the presence of large amounts of partially melted material having a characteristic dotted eutectic structure as shown in Fig. 31, makes the diagnosing, in "post mortem" examinations, of the trouble arising from this, comparatively easy. These steels are also much harder to forge than the lower carbon steels and as the reheating temperature may not be raised unduly, owing to the danger of burning, the hot working of such steel is, therefore, much more difficult than that of the lower carbon steels.

From a theoretical point of view, however, their most interesting feature lies in the fact that when quenched from very high temperatures, 1,200° C. or thereabouts, they do not harden, owing to the fact that the austenite which exists at these high temperatures is retained as such on quenching and does not change into martensite. During the quenching of ordinary steels or of the lower carbon

varieties of stainless steel, the changes which would normally occur at the Ar.1 point during slower cooling are not entirely suppressed though the separation of the carbide of iron and of the iron into microscopically visible particles is, of course, entirely prevented. The part of the change which still occurs, in spite of the utmost rapidity of quenching, concerns the iron itself. The power which the iron in the pearlite acquires, when heated to the Ac.1 point, of dissolving the alternating lamellae of carbide, is due to a rearrangement in its own crystalline structure. Carbon is almost completely insoluble in the ordinary form of iron existing at atmospheric temperatures, but with the change in its crystalline structure, which takes place when austenite is formed, iron acquires the power of dissolving a limited amount of carbon. There are other differences in the physical properties of the two forms of iron; thus the ordinary low temperature variety, which for convenience is designated α -iron, is strongly magnetic, while the high temperature type, known as γ -iron, is practically non-magnetic. During the slow cooling of ordinary steel, or of stainless steel, the Ar.1 point marks the change of the γ -iron of the austenite to α -iron with the coincident precipitation from solution of carbide of iron. By rapidly quenching the stainless steels considered up to now, the precipitation of the carbide is prevented but, as with ordinary carbon steels, the change of the γ -iron to α -iron cannot be suppressed and under such conditions this part of the change takes place at about 300° C., leading to the production of martensite, which incidentally is magnetic, from the austenite. In pure iron the change from the gamma form to the alpha takes place at about 900° C., and in such material it is not possible, even by the most rapid quenching, to prevent this change taking place. In the presence of carbon, the γ -form containing this element in solution remains stable down to the Ar.1 point at about 700° C. on slow cooling and is retained to still lower temperatures on quenching. The presence of chromium in the steel lessens still further the tendency of the γ -iron to change to the α -form on cooling, so that when both chromium and carbon are present in sufficient amounts in solution in the iron, the stability of the γ -form is increased to such an extent that it may be preserved unchanged during cooling to ordinary temperatures. In order that this may take place,

both the chromium and carbon must be in solution in the iron and this only occurs when the steel containing them is heated to high temperatures; hence when such steels are quenched from a series of gradually increasing temperatures above A_{c1} , they at first gradually get harder, reaching Brinell hardness numbers of 600 and upwards when quenched from about $1,000^{\circ}\text{C}$. The structure of

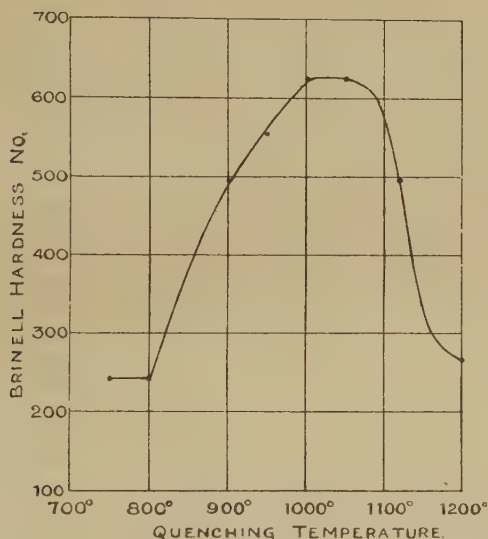


FIG. 32. Brinell hardness numbers obtained on quenching steel containing 0.96 per cent. carbon and 13.1 per cent. chromium from the temperatures indicated.

such quenched samples consists of martensite together with large amounts of free carbide. When, however, the quenching temperature reaches a figure which is generally between $1,100^{\circ}$ and $1,200^{\circ}\text{C}$., the Brinell hardness number of the quenched sample suddenly falls to quite a low figure. The sample also acquires a characteristic microstructure and, in addition, is found to be non-magnetic. The hardness numbers obtained by quenching such a steel, containing 0.96 per cent. carbon and 13.1 per cent. chromium, from a series of temperatures are plotted in Fig. 32 and enable one to visualise the striking changes in the hardness value which are produced as the quenching temperature of such a steel is raised.

The carbon content required to produce austenite varies with the amount of chromium present in the steel; with about 13 per cent. of the latter, however, the martensite in a specimen quenched from $1,200^{\circ}\text{C}$. will be partially replaced by austenite when the carbon reaches about 0.5 per cent. and the steel will be completely austenitic, after a like treatment, with 0.7 per cent. carbon or more.

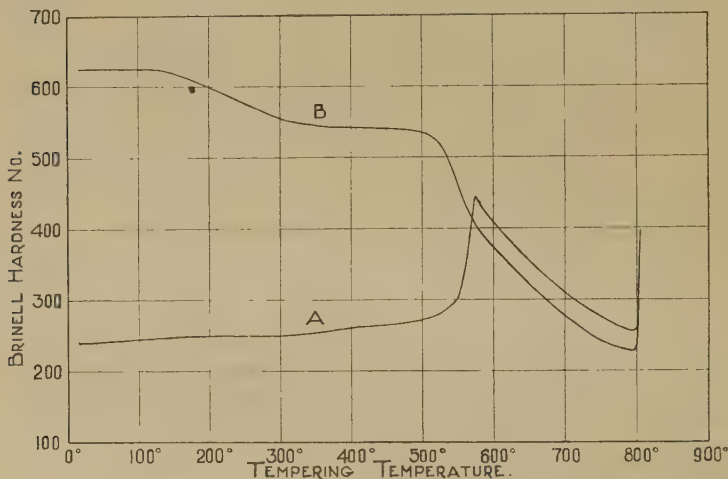


FIG. 33. Brinell hardness numbers obtained after tempering steel containing 1.01 per cent. carbon and 11.8 per cent. chromium.

Curve A—Samples previously quenched from $1,200^{\circ}\text{C}$.
 Curve B " " " " $1,000^{\circ}\text{C}$.

A further point of interest with such austenitic steels lies in their behaviour on tempering. No appreciable effect is produced until the tempering temperature reaches about 550° to 600°C . At this temperature, the change from austenite to martensite, which was suppressed when the material was quenched from $1,200^{\circ}\text{C}$., now takes place and, consequently, the material hardens when so tempered. Thus curve A in Fig. 33 represents the Brinell hardness numbers of samples of such a steel after tempering at gradually increasing temperatures and makes evident the very material increase in hardness obtained after tempering at about 600°C . The structure of such "hardened" samples consists of martensite, though generally this is accompanied by more or less troostite because the martensite formed by the

tempering operation is itself very easily changed, as will be apparent from the rapid fall in hardness which occurs when the tempering temperature is raised somewhat higher (see Fig. 33).

On the other hand, when these high carbon steels are quenched from lower temperatures, e.g., $1,000^{\circ}\text{C}$. or thereabouts, giving Brinell hardness numbers of 600 or so, they consist of martensite, together with free carbide, and, on tempering, behave in a similar manner to the lower carbon steels. This is illustrated by curve B in Fig. 33, which was obtained from the same steel as curve A, but the samples had been previously quenched from $1,000^{\circ}\text{C}$. instead of $1,200^{\circ}\text{C}$. A comparison of these two curves also illustrates another effect of varying quenching temperature on stainless steel. It will be noticed that the samples quenched from $1,200^{\circ}\text{C}$. are harder than those quenched from $1,000^{\circ}\text{C}$. when both are tempered at temperatures above 600°C . This manifestation of a type of "red-hardness" is frequently produced in all high chromium steels; it will be referred to later in connection with the mechanical properties of the steel.

As typical photographs of such high carbon steels, Figs. 28, 29 and 30 are included. Fig. 28 represents the structure of a steel containing 1.01 per cent. carbon and 11.8 per cent. chromium, when hardened and fully tempered (Brinell hardness number 241), and illustrates the large amount of carbide in such a steel; the same steel quenched at $1,000^{\circ}\text{C}$. had a Brinell hardness number of 627 and the structure shown in Fig. 29; even at this temperature there is much carbide remaining undissolved. The importance of the effect of this carbide on the resistance of such material to corrosion will be indicated later. Fig. 30, obtained from a steel with 0.67 per cent. carbon and 14.1 per cent. chromium, after quenching from $1,200^{\circ}\text{C}$., is typical of the appearance of the constituent austenite in these steels.

Macrostructure and Ingot Heterogeneity. In the preceding pages, the changes produced by different conditions of heat treatment on the structure of stainless material have been considered on the tacit assumption that such material was homogeneous in character, i.e., that the chromium, carbon and other elements present in the steel were evenly distributed through the iron, or, at any rate,

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in a sufficiently even manner as to approximate to a homogeneous condition for practical purposes. It is important, however, to see whether such a condition actually exists and if not, to what extent the structure of the steel departs from homogeneity.

It is well known that when ordinary carbon steel solidifies from the fluid condition, the portions of each separate crystal which freeze out first contain a smaller percentage of dissolved impurities, such as carbon, silicon, manganese, phosphorus, than the fluid steel from which they separate, and that, as freezing gradually progresses, material containing a gradually increasing amount of such impurities is deposited, the portions which finally freeze being much more impure than the original fluid metal. During and after freezing, however, diffusion takes place rapidly with regard to the carbon, so that the original distribution of this element in the solid material is to a very great extent obliterated. The other elements present, however, diffuse much more slowly, if at all, and hence the original crystalline structure produced during the freezing process may be shown in ordinary steels by the use of special etching reagents which attack the steel in a manner depending on the concentration of these dissolved impurities. By the use of such reagents as, for example, the various "copper" reagents developed by Rosenhain, Stead, Le Chatelier and others, or the still more striking method of macro-etching described by Humphrey,* the purer dendrites which solidified first are attacked in preference to the more impure areas and, as a result, one obtains a dendritic structure similar to Fig. 34, which shows very clearly how the crystalline mass of the steel was built up. Etching the same section with the ordinary reagents used in the microscopic examination of steel, such as a five per cent. solution of picric acid in alcohol, reveals merely the distribution of carbon in the steel when cold and, as the carbon during and immediately after solidification has diffused, producing an austenite practically homogeneous with respect to this element, which has afterwards split up at the critical changes into pearlite and ferrite or cementite, the patterns produced by the two types of reagents often bear little apparent relation to each other. During any subsequent heat treatment operations, the original distribution of the

* *J.I.S.I.*, 1919, I, 273.



FIG. 34. Dendritic structure of ordinary carbon steel ingot.

Plate VIII.

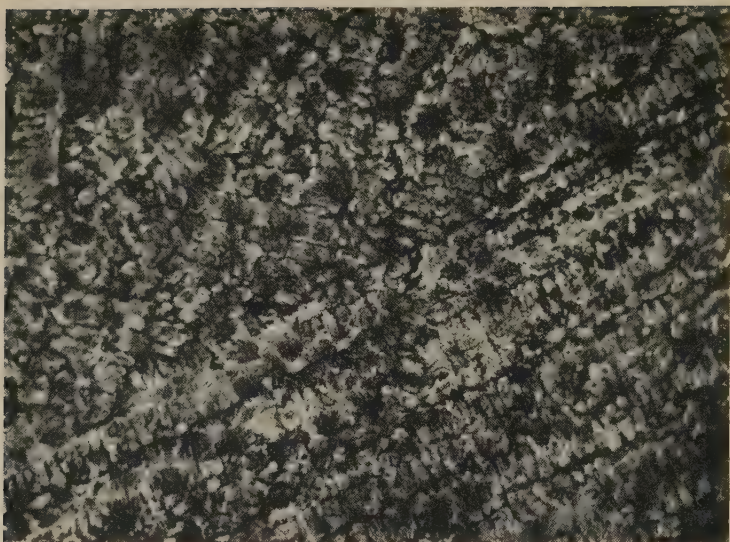


FIG. 35. Dendritic structure of cast sample of stainless steel (0.42 per cent. carbon), slowly cooled after casting. $\times 50$.

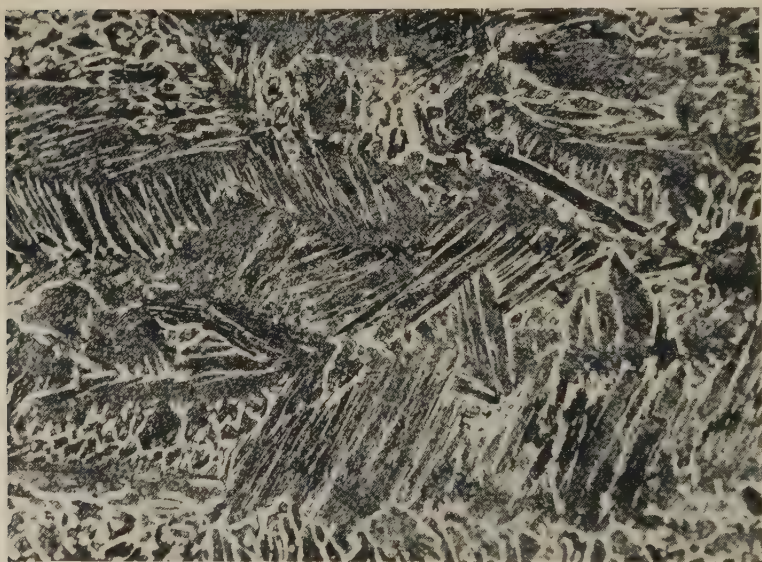


FIG. 36. Dendritic structure of ingot of stainless iron containing 0.07 per cent. carbon. $\times 50$.

impurities other than carbon is practically unaffected. Even rolling or forging operations do not remove this pattern but merely distort it to a greater or less degree. On the other hand the carbon distribution, as shown by the ordinary pearlite and ferrite or cementite structure, is modified every time the material is heated and cooled through the change points. In any piece of ordinary carbon steel, therefore, there are two structures more or less independent of each other; the one shows the state and distribution of the carbon in the steel, and forms the ordinary microstructure; the other indicates the original crystallisation of the ingot, produced on solidification and more or less distorted by subsequent mechanical work, and is generally referred to as the "macrostructure" since its pattern is fairly coarse and visible to the unaided eye.

In stainless material the presence of the large amount of chromium so retards the diffusion of the carbon that the distribution of this element in a cast sample of the steel, when cold, outlines the original dendritic structure produced on solidification, and not only so, but this structure persists to a marked extent even through the operations of forging and rolling. In samples, such as ingots or castings, which have been cooled down after casting at a sufficiently slow rate to soften the material completely, the original dendritic structure is shown very markedly by the distribution of the carbide. Thus Fig. 35 shows the structure obtained with such a sample containing 0.42 per cent. carbon and 11.3 per cent. chromium; it will be seen that the dendrites which solidified first contain less carbide than the interdendritic filling which froze later. A similar sample cooled quickly after casting consisted of a mixture of martensite and austenite, the former occupying the position of the dendrites while the latter occurred in the interdendritic filling, the carbon concentration there being sufficiently high to cause the complete suppression of the change points on rapid cooling and the consequent retention of austenite. Similar dendritic structures may be obtained with the low carbon stainless iron, thus Fig. 36 shows the structure obtained from an ingot containing 0.07 per cent. carbon and 11.7 per cent. chromium and consists of ferrite and martensite. This dendritic structure is very persistent even after drastic heat treatment. As examples of this Figs. 37 and 38 are of

interest; the former represents the structure of a sample similar to that represented in Fig. 35, after annealing for four hours at $1,100^{\circ}\text{C.}$; the latter shows that of a bar, $1\frac{1}{2}$ inches diameter, of similar analysis to the cast sample described above, after the forging and rolling operations necessary to reduce it from an ingot 12 inches square. In both cases the dendritic structure is perfectly evident. Both these samples are certainly in the annealed condition, and the structure obtained by such treatment emphasises the distribution of the carbide in a much more marked manner than when the material is hardened or hardened and tempered; the rather high carbon which the samples contain also helps in retaining the original heterogeneity; however they serve to emphasise the effect of the chromium in retarding the diffusion of the carbon in the steel.

It will be evident from the examples given above that there is likely to be evidence of a certain degree of heterogeneity in all samples of stainless steel. During the rolling or forging operations, the original dendritic structure with its variations in composition is distorted and drawn out to a greater or less extent into fibres or thin plates depending on the section of the bar into which the material is being worked. Each reheating for mechanical work affords opportunity for diffusion to take place to some extent, while the actual forging and rolling, by reducing the cross sectional area of the original dendrites, reduces the distance through which diffusion has to take place and thereby helps it considerably. As far as the author is aware no estimation of the amount of heterogeneity, due to the original dendritic structure, existing in a rolled or forged product of stainless steel has been made and although it can be detected in different ways, even in material which has been reduced in cross section to a considerable extent, it is probable that its amount is considerably less than it was in the ingot form.

The presence of this heterogeneity may be shown very strikingly by quenching the steel from a temperature not quite high enough to dissolve the whole of the carbide, in which case in a longitudinal section, the carbide remaining out of solution will tend to be arranged in chains or streaks separated by other streaks which are practically free from carbide. It may also be disclosed by slowly cooling the

Plate IX



FIG. 37. Similar sample to that shown in Fig. 35 after annealing for four hours at $1,100^{\circ}\text{C}.$; the dendritic structure is still prominent. $\times 50$.



FIG. 38. Remnants of the original dendritic structure visible in a rolled bar, $1\frac{1}{2}$ -ins. diameter, of stainless steel. $\times 100$.

steel from a similar temperature; in this case the streaks in which the carbide had been taken completely into solution will have a pearlite structure while the alternating streaks, where some carbide remained undissolved at the annealing temperature, will contain globular carbide.

It is doubtful what effect these remnants of the original structure have on the properties of the rolled or forged product because such effects as they might have are also produced in probably much greater degree by slag and other non-metallic inclusions in the steel. Like other things, however, which at first sight appear to be entirely objectionable, the extremely slow diffusion of the various elements present in stainless steel, which allows the original heterogeneity produced during solidification to be preserved to a greater or less degree, has some very distinct advantages for what may be described as instructional purposes. Thus it emphasises the fact, by making it more easily visible, that all forged or rolled steel, stainless or otherwise, possesses a "fibre" or "grain" which is quite as much a feature of steel as it is of wood, though it is not always so prominent to the eye in the metal. This fibre is probably mainly due to the presence of minute particles of slag or other non-metallic inclusions which are mixed up with the steel. These, existing in the ingot as more or less rounded particles, are drawn out during forging or rolling operations into threads or plates, imparting to the worked product a fibre which should be taken into account quite as much as is the fibre in the working of wood.

Again, because the original crystalline characteristics of the ingot are not completely obliterated by heat treatment or by mechanical work, it follows that these characteristics can be recognised in the bars, forgings, stampings or other articles prepared from the ingot and thus help in correlating observed properties of the finished material or of its behaviour during hot working with ingot characteristics. In the same way, the distortion of this original dendritic structure during forging operations produces a recognisable pattern in the forged article; a study of this pattern often provides much useful information as to the methods of forging employed. In these respects the behaviour of stainless steel does not differ, except in degree, from that of ordinary steel or of the more common alloy steels. In all these steels the

remnants of the ingot structure can be used in a similar manner; in the stainless steel, however, as with some other alloy steels, the lessened rate of diffusion of the carbon allows the original heterogeneity with respect to this element to persist in a marked degree and hence, reinforcing the effects of the differences due to other elements, enables the distorted ingot pattern to be more readily shown. It is perhaps, in a way, fortunate that this is the case with stainless steel because one of the most useful elements to the steel metallurgist in indicating ingot characteristics, sulphur, does not function so well in this respect in this metal. In ordinary steel, sulphur exists as minute particles of manganese sulphide mechanically mixed with the steel; a study of the distribution of these particles, easily carried out by means of a "sulphur print,"* gives much useful information as to ingot conditions. With stainless steel, sulphur prints are much less readily obtainable; even when stronger acid and a longer time of contact are used, the sulphide image sometimes fails to develop. Apparently the sulphur exists in stainless steel in a form not readily attacked by acids; beyond the fact, however, of the difference in behaviour of the sulphur test in ordinary and stainless steels little is known about the mode of existence of the sulphur in the latter; obviously, however, it is not present in the same form as in ordinary steels.

Thermal Curves. The absorption and evolution of heat occurring respectively at the Ac.1 and Ar.1 changes have been used for a long time by metallurgists as a means of locating the exact temperatures at which these changes occur. They may be similarly used in connection with stainless steel, and a study of the results thereby obtained provides interesting and useful data in connection with the heat treatment of the steel.

Many elaborate forms of apparatus have been devised for the purpose of obtaining such thermal data on both ordinary carbon steels and alloy steels. For experimental work, where great accuracy in temperature measurement

* Such a print is obtained by pressing a piece of ordinary photographic "bromide" paper, previously soaked in water containing 2 or 3 per cent. of sulphuric acid, in contact with a smoothly filed or ground surface of the steel. Thirty to sixty seconds' contact is generally sufficient for ordinary steels. With stainless steel a stronger acid solution, up to about 10 per cent., may be used and a contact time of 5 to 10 minutes may be necessary.

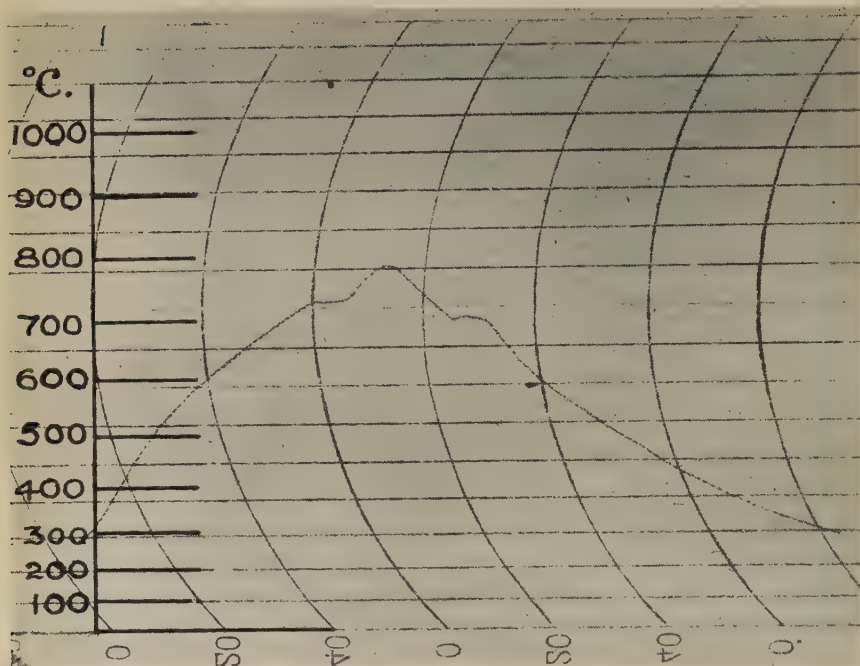


FIG. 39. Heating and cooling curves of ordinary tool steel obtained on works recorder.

and the ability to detect minute changes in heat evolution or absorption are required, such elaboration of apparatus may be desirable; for ordinary works purposes, however, an automatic temperature recorder, of which there are several satisfactory patterns on the market, reading to five degrees Centigrade furnishes most, if not all, of the data required. Such a recorder gives a curve in which temperature is plotted against time. If such a recorder is connected to a thermocouple inserted in a hole drilled in a sample of steel and the latter placed in a furnace, the temperature of which is being raised at a uniform rate, the temperature of the sample will increase uniformly so long as no change takes place in the steel itself; hence the curve drawn by the temperature recorder will be smooth and will show no perturbations. When, however, the Ac.1 point is reached, the change which then takes place absorbs a considerable amount of heat and hence, for a short interval, the steel either does not get any hotter or else increases in temperature at a slower rate than before, thus producing a break in the curve obtained from the temperature recorder. Similarly on cooling, the heat evolved by the steel on passing through the Ar.1 change temporarily delays the cooling of the sample until the change is completed. A record so obtained from a piece of ordinary carbon tool steel is shown in Fig. 39 and will serve as a standard with which the curves similarly obtained from stainless steel may be compared. It will be noted that the absorption and evolution of heat at Ac.1 and Ar.1 are both very sharply defined and that the temperatures at which they occur agree with those given for these points when the changes in structure occurring at them were discussed (page 26). A heating curve obtained in the same manner from a sample of stainless steel gave the result shown in the left-hand portion of the curve in Fig. 40. In this case the Ac.1 change occurs near 800°C. , but otherwise the curve obtained is similar to that from the ordinary steel, except that the absorption of heat is possibly not so sharply defined but tends rather to spread over a range of a few degrees than to occur at one temperature. This curve is typical of what may be obtained from stainless steel containing 0.3 per cent. carbon or thereabouts; the actual temperature obtained for the Ac.1 point with any particular specimen depends on the composition of the latter more particularly with regard to silicon and

nickel, the former element raising the temperature of the Ac.1 change and the latter lowering it.

In addition, with any particular steel, the temperature at which the Ac.1 point occurs is affected slightly by the rate at which the sample is heated, a faster rate tending to give a somewhat higher temperature, and also by the previous thermal history of the sample. In the latter case, the Ac.1 point is likely to occur a few degrees higher in a sample which has previously been annealed than in a piece of the same steel in the hardened or hardened and tempered conditions. This effect, which is probably connected with the relative sizes of the carbide particles given by the two types of heat treatment, may be seen in Fig. 40. Prior to taking the first heating curve in this diagram, the sample had been hardened and tempered; after the subsequent slow cooling, producing the Ar.1 point at 760°C. , the material was of course, in the annealed condition and in the second heating curve, which followed, the Ac.1 point occurred at 802°C. instead of 798°C.

In the case of the changes occurring on cooling, however, the rate at which the sample is cooled plays a very important part, as will be evident from what has already been stated when discussing the microstructural changes. The results obtained may be summarised as follows: If the steel is cooled from above the Ac.1 change point at a sufficiently slow rate to soften it completely (i.e., to give either a pearlitic structure similar to Figs. 2, 3 and 4, or the granular type, illustrated in Fig. 17, obtained under similar cooling conditions from temperatures at which all the carbide had not been taken completely into solution) an evolution of heat is produced in the range 770° to 700°C. approximately. The actual temperature at which this evolution of heat occurs depends on the rate of cooling employed and the maximum temperature to which the steel was heated before cooling. A slower rate of cooling tends to raise the temperature at which the change occurs, while raising the initial temperature from which the steel was cooled tends to lower the change point. It follows from this that the highest temperature at which the evolution of heat can occur is most likely to be obtained by heating the sample initially to a temperature only just above that of the change point on heating and then cooling slowly therefrom. Under such

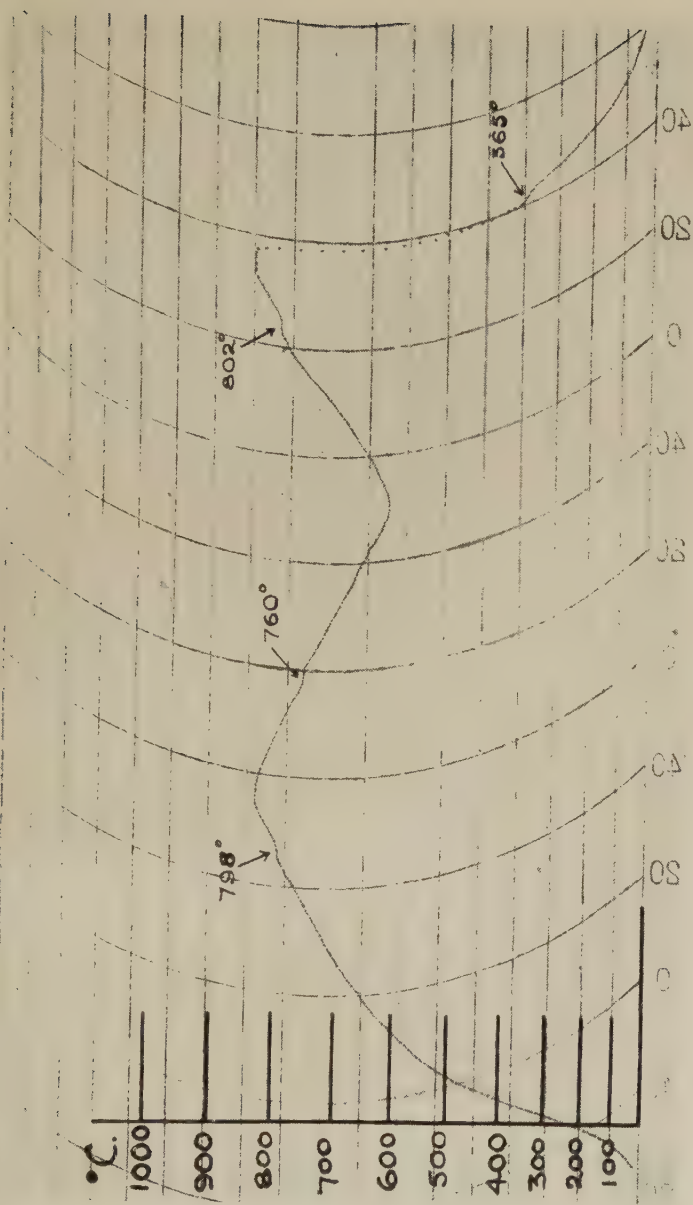


FIG. 40. Heating and cooling curves of stainless steel obtained on works recorder. (See page 52).

To face page 52.]

conditions, the evolution of heat is very well marked and occurs at about 760°C , or slightly higher. On increasing the rate of cooling, while still retaining the same initial temperature from which the cooling commenced, the temperature at which the evolution of heat occurs falls slightly, the critical change, however, being still well marked. This continues until a cooling rate fast enough to cause the steel to commence to harden is reached. The evolution then becomes less defined and occupies a range of temperature while a further change point occurring at about 400°C . becomes visible. With still faster rates of cooling, the upper point becomes less marked, and occurs at still lower temperatures, while the lower point becomes more marked. At the same time, the hardness of the samples after cooling increases rapidly. Finally, the upper point disappears entirely and one obtains only the lower point, in the range 350° to 400°C .

As an illustration of this, the following table gives the results obtained on a steel containing :—

Carbon	... 0.34 %
Silicon	... 0.12 %
Manganese	... 0.24 %
Chromium	... 11.2 %

cooled at different rates from 860° . The rates of cooling were measured by taking the time occupied in cooling from 850° to 550°C .

Time of Cooling.	Temperature of Critical Range.					Brinell Hardness Number After Cooling.
54 min.	766°	170
15 "	748° to 742° C.	179
13 "	741° to 735° C.	179
11 "	{ 720° to 700° C.	255
	{ 410° C.					
9 "	{ 715° to 700° C.	277
	{ 385° C.					
8½ "	{ 700° to 665° C.	311
	{ 385° C.					
6½ "	{ Slight, between 700° and 600° C.	332
	{ 405° C.					
3½ "	360° C.	387
1½ "	350° C.	402

When samples are cooled from a higher initial temperature, a similar sequence is obtained except that the rates of cooling necessary to obtain similar effects become progressively slower as the initial temperature of cooling is raised. This will be apparent from Fig. 18 and the descriptions with regard to the structural changes which were given earlier in the chapter.

The types of cooling curves obtainable on a works recorder are shown in Fig. 40: in the first cooling curve depicted therein, the sample was slowly cooled in the furnace and gave a well-defined Ar.1 point at 760°C . For the second cooling curve, the sample ($\frac{3}{4}$ -in. diameter and 1-in. long) was withdrawn from the furnace at a temperature of 840°C . and allowed to cool freely in the air, producing the "lowered" Ar.1 point at 365°C .

The temperature at which the "lowered" Ar.1 point occurs, that is, the one obtained at 400°C . or below when the steel is cooled at a sufficiently fast rate to cause it to harden more or less completely, depends on the maximum temperature to which the steel was heated before cooling. The higher this maximum temperature is, the lower the position of the change point. Thus, in the examples quoted on page 53, the lowered change point occurred between 350° and 400°C ., the maximum temperature to which the steel was heated prior to cooling being 860°C . When the same steel was cooled from $1,200^{\circ}\text{C}$., the lowered change point occurred in the range 250° to 275°C .

The significance of the change points occurring in these two ranges of temperature, approximately 600° to 750°C . and 250° to 400°C ., is readily apparent from a microscopical point of view. That occurring in the upper range marks the breakdown of the austenite with the formation of pearlite or of its finer varieties, sorbite and troostite. The lower critical range, on the other hand, marks the formation of martensite from the austenite. When the rate of cooling is such that evolutions of heat occur in both ranges of temperature, a structure consisting of a mixture of martensite and troostite is produced, the proportions of the two constituents depending on the relative amount of the heat evolutions in the two ranges of temperature.

MANUFACTURE, WORKING, AND TREATMENT
OF STAINLESS STEEL

CHAPTER III

MANUFACTURE, WORKING, AND TREATMENT OF STAINLESS STEEL

Stainless steel and iron are generally made in the basic-lined electric furnace. Material with a carbon content of about 0·2 or 0·3 or above can be made in the crucible furnace, but if a lower carbon material than this is required the electric furnace is practically essential. Before adding the chromium alloys, the carbon content of the electric furnace bath is reduced to about 0·10 per cent., or below for stainless iron; afterwards the utmost precautions have to be taken to avoid contamination with carbonaceous matter, which is greedily absorbed by the molten metal, especially when the lowest carbon material is being made. If stainless steel scrap forms part of the charge, some of the chromium is oxidised into the slag during the early stages but, by careful control, the loss can be minimised.

It is of the utmost importance that the bath and slag are in good condition before the metal is tapped from the furnace. Steel which is not perfectly killed leads to blow-holes, with their accompanying "spot segregates," in the steel, and such steel is distinctly less resistant to corrosion than sound material of similar analysis. In the same way, the molten metal should be as free as possible from slag inclusions, as such slag particles may form centres of corrosion.

The type of ferrochrome needed to bring the chromium content of the bath to the required percentage will obviously depend on the carbon content required in the finished material and also on the actual carbon and chromium contents of the bath previous to the addition of the alloy. For the very low carbon stainless iron, only the carbonless alloy is of any use. For the higher carbon steels, e.g., the cutlery quality containing about 0·3 per cent. carbon, the grade of ferrochrome containing 0·5 to 1·0 per cent. carbon can generally be used.

Owing to the high cost of low carbon ferrochrome and especially of the practically carbonless variety required for the production of stainless iron (although improvements in the manufacture of these alloys, resulting in a lessened cost of production, have been and are being made), numerous attempts have been made to introduce the necessary chromium at a less cost. One of the most obvious methods is to use chromite, an ore of chromium consisting largely of its oxide, directly in the steel-making furnace and effect its reduction in the furnace by means of such reducers as ferro-silicon or aluminium. Since chromite itself is comparatively cheap and the actual reduction by means of silicon or aluminium is quite feasible, the process has obvious attractions from the point of view of cost. Unfortunately, however, there are several drawbacks which have not been completely overcome. The ore, chromite, is naturally not as free from impurities as the purified alloy manufactured from it, and hence it is more likely to cause trouble than the purer alloy by the introduction of such impurities into the bath or slag. In addition, a rather voluminous slag, which in the case when silicon is used as a reducer is likely to attack the banks of the furnace, is produced which causes some trouble and, incidentally, expense in dealing with. From the point of view of the product, however, a more serious trouble will arise unless the reaction in the furnace is very carefully controlled. Unless it is watched very carefully, an excess of silicon or aluminium may be absorbed by the molten steel and, as will be seen later, both these elements have an effect on the mechanical properties of the finished product which is very undesirable for most engineering uses of the material. In addition to this, of course, there is much more likelihood of variation in the final composition of the finished steel when the chromium is introduced by these methods than when it is added in the form of a definite weight of alloy of known composition.

The idea of using silicon or its alloys as a reducing agent for the production of chromium alloys with a low carbon content is not by any means new, thus patents covering the use of ferrosilicon for the production of such low carbon alloys, ferrochrome being quoted as an example, were taken out in the United States of America in April, 1907, by E. F. Price and in May, 1907, by F. M. Becket. In February,

1916, one of the author's colleagues, Mr. F. A. Melmoth, successfully produced material containing 0.13 per cent. carbon and 12.3 per cent. chromium in a twenty cwt. electric furnace, the chromium being supplied entirely by the reduction of chromite by ferrosilicon in the furnace.

One of the handicaps to the more general use of stainless steel is its greater initial cost compared with that of ordinary steel. The primary cost of an article is the one most frequently considered and although it has been found in practice that for many purposes the relative cost of stainless steel, that is, its cost in terms of service and working life, is considerably less than that of ordinary steel, this point of view is often not sufficiently appreciated by potential users. A lessened cost of production is therefore to be desired. The methods mentioned above are worthy of attention in this respect, and although it would appear that, owing to difficulties such as those outlined above, they have not attained complete success, nor is it certain that the reduction in cost is so great as has been suggested, it is possible that more efficient control of the process, obtained as a result of greater experience, will remove the difficulties. If, as a result, the cost of the manufacture of stainless steel is thereby greatly cheapened, there is little doubt its application will increase rapidly.

The tapping of stainless steel from the furnace into the ladle and the teeming of the metal into the ingot moulds do not differ in any essential respect from the corresponding practices with ordinary steel. Owing, however, to the greater cost of the stainless material and to the trouble caused in later operations in manufacture and also after the material is put into use, by surface defects or by internal unsoundness, it is of the greatest importance that every care and precaution be taken to ensure the ingots being as free as possible from avoidable defects. The extra expense caused by such details as the use of properly designed ingot moulds with feeder heads, so as to eliminate piping from the body of the ingot, and the careful inspection of moulds to see that their surfaces are in good condition, is negligible compared with the saving obtained by their use. In the same way the superior ingot surface obtainable in general by "bottom casting" makes it worth while to use this method providing, of course, precautions are taken to see that inclusions of ganister, firebrick, or

other extraneous matter are not introduced through carelessness.

With the exception of the lowest carbon variety, stainless steels air harden intensively on cooling from high temperatures. Care must therefore be taken with the cooling of the hot ingots, otherwise serious cracks may form as a result of too rapid or uneven cooling. In addition to this, if the material becomes hard when cold it is then much more susceptible to cracking during after treatment. Cracks are produced much more easily in such hard material than in soft material by rough handling or grinding. The latter, if done rashly, causes local heating and the expansion due to such heating may easily set up sufficient stress in the neighbourhood of the heated area to cause cracks to form in hard non-ductile material. Similarly, surface defects are much more dangerous as starting points of cracks when they occur in hardened steel. Finally, when the ingots have to be reheated for forging or rolling operations, much more care is required to prevent cracking occurring if they are in the hardened condition.

The most certain way of avoiding or, at any rate, greatly minimising these troubles is to take care that the material is never allowed to become hard either in the ingot form or between the various operations of reheating and forging or rolling. As this point is of the utmost importance in the manufacture of stainless steel it is necessary to emphasise it thoroughly, and no excuse is required for going into some detail with regard to the methods of preventing the trouble.

If the material is allowed to cool, this should be done in such a way that the air hardening tendency is completely suppressed, the material, when cold, being then in the pearlitic or annealed condition. For this purpose the hot ingots, blooms, billets, or whatever form the material is in, may be allowed to cool slowly in some form of furnace or firebrick-lined pit. With stainless steel the carbon change point occurs generally in the range 600° to 750° C. on slow cooling. The material should therefore be allowed to cool slowly over this range of temperature. The rate of cooling down to 750° C. is immaterial, but from 750° C. to 600° C., the range of temperature mentioned above, the rate of cooling should not be faster than 50° an hour at the most. If this has been done efficiently, the material may then be air-cooled with perfect safety.

Although the method of cooling in a firebrick-lined pit may be satisfactory when the material is in the form of very large pieces which retain their heat for hours, it is an unsatisfactory method for small billets, bars or forgings which cool more quickly. A far better method for such small sized material is to charge the hot forgings or bars into a furnace which is kept in the range of temperature in which the carbon change occurs on slow cooling and hold them there for a sufficient length of time for the change to take place. After this has occurred, the material can be air cooled or even quenched out in water and will still be quite soft.

In practice, it is better to use a range of 600° to 700° C. for the furnace temperature, since most samples of stainless steel contain small amounts of nickel, and this element lowers the maximum temperature at which the change point can occur. It is obviously no use soaking the steel at a temperature above the highest at which the carbon change can possibly take place, while on the other hand, the use of a temperature 50° or 100° C. below this highest value is perfectly successful.

As a general rule, soaking for about an hour in this range of temperature is sufficient to cause the carbon change to take place; it is advisable, however, to have some means of knowing when the red hot material has actually changed from austenite to pearlite. For this purpose, one may make use of the fact that the steel becomes magnetic when this transformation takes place. The steel should be tested with a small permanent magnet and should be allowed to stay in the furnace until it is distinctly magnetic while it is red hot. It is, of course, no use applying the magnet test after the steel has gone cold, since it is then magnetic whether hard or soft.

It should be noted that the magnet test mentioned above, while perfectly satisfactory for stainless steel, is not a reliable criterion of the annealing of the low carbon material, stainless iron. With this material, separation of free ferrite occurs during slow cooling at a temperature above that of the carbon change point, in a similar manner to the separation of free ferrite in ordinary mild steels. The free ferrite which has thus separated out undergoes the Ar.2 magnetic change at a temperature of about 650° to 680° C., and hence the material will be decidedly magnetic immediately after this change has occurred, although the remainder of the material

(which contains the carbon) is still in the form of non-magnetic austenite and therefore capable of forming either martensite or pearlite, depending on the succeeding rate of cooling. With such mild material, however, the hardness obtained on air cooling is quite low (generally of the order of 230-320 Brinell) and hence the material is much less susceptible to cracking and other defects liable to be produced in material which air hardens intensively.

This method of annealing stainless material by soaking in the range 600° to 700° C. has proved of great value in the manufacture and working of the material, especially in the form of small articles. During the production of small drop stampings, for example, the hot stampings should be charged, as soon as the stamping operation is completed, into the furnace kept at 600° to 700° C., and allowed to soak, after which they may be air cooled with perfect safety. It is of no consequence if the stampings are actually below 600° C. when they are charged, providing they are not lower than about 350° C., except that the process will take longer owing to the time taken to reheat them to the necessary range of temperature. If the temperature is below about 350° C., the lowered carbon change point, resulting in the production of hardened material, may have taken place partially or completely, with the consequent liability for cracking to occur. For material cooled to such a temperature, reheating to $600^{\circ}/700^{\circ}$ C., followed by soaking at that temperature would result, of course, in tempering the hardened steel.

Since troubles due to cracking become evident when the material becomes cold, obviously one way out of the difficulty is to prevent the articles becoming cold between successive stages in the working of the steel; thus the material may be charged back into the reheating furnace immediately one stage of the forging operation is completed (for reheating for the next operation) whilst the bloom, billet, or whatever form the material is in, is still red hot. As a preventative of cracking, this method, when properly carried out, is satisfactory. It has the disadvantage, however, that there is no opportunity (since the material does not become cold between these successive operations) for examination and removal of defects, e.g., by chipping or machining, between the forging operations.

This method is obviously of value in dealing with ingots

when conditions will allow it to be applied. Owing to structural characteristics, stainless steel, like other steels, will probably crack more easily in the ingot form than after being worked, so that, if the rolling or forging procedure will allow it, it is an obvious advantage to keep the ingot hot until it has been forged or rolled (and therefore not give it any chance of cracking) rather than to cool it even under conditions which would soften it perfectly. It is well to remember that even when fully annealed, cold ingots of stainless steel should be treated with as much care as an ingot of, for example, file steel.

The forging or rolling of stainless material is carried out in much the same way as that of ordinary steel, except that the stainless material needs more care. It will not stand so rapid a reduction in cross-section as will ordinary steel, and it is considerably harder than this material. As regards the latter point, stainless iron probably forges as easily as ordinary steel containing about 0.4 per cent. carbon; forging becomes more difficult as the carbon increases, so that the harder varieties of stainless steel, with carbon about 0.4 per cent. or over, are almost as difficult to forge as high speed steel. The difference between stainless iron and the grade suitable for cutlery (carbon about 0.3 per cent.) is illustrated by the fact that four to six times as much work may be done on the former material at one heat as on the latter. With regard to small articles, stainless iron may be forged quite easily by hand into such complicated objects as spurs, but a power hammer is indispensable for large articles or for those made from the harder varieties of stainless steel.

Stainless iron and steel may be forged quickly and by rapid blows between temperatures of 1,200° and 900° C., without danger of splitting. Below 850° to 900° C. it stiffens up considerably, and if attempts are made to deform it forcibly with heavy blows, it will be unduly stressed and will probably crack.

It is also not advisable to attempt to continue the hammering of small forgings, such as knife-blades, until they are almost cold, with the idea of making them springy. Material so treated, being more or less cold worked, is unreliable and more likely to corrode or rust than material of similar composition normally treated.

In the commercial forging of small articles on which

successive forging operations are carried out, probably on different machines, care must be taken that the forgings are not allowed to cool off on the floor between these successive operations, otherwise cracking will certainly occur. This danger has already been dwelt upon but, at the risk of being thought to labour the point unduly, it may be emphasised again by alluding to the difficulties which arose in the early days of stainless cutlery manufacture. At that time much trouble was experienced with cracked blades owing to the fact that after each of the forging operations (mooding, goffing, bolstering and tanging) the blades were allowed to become more or less cold. The steel consequently hardened at each operation and the effect was similar to what would have been produced with blades of ordinary cutlery steel had these been quenched out in water after each of the above operations. By arranging, however, that the material is kept hot between each forging operation or if allowed to cool, is cooled in such a way as to soften it, the difficulty with cracked blades may be considerably reduced. In connection with this, it may be noted that hardening cracks are much more likely to be formed after the article has air cooled below about 300°C . than above this temperature.

Stainless steel and iron may be drop stamped between temperatures of $1,000^{\circ}$ to $1,200^{\circ}\text{C}$. Whenever possible, it is better to use stainless iron or the milder types of the steel rather than the higher carbon grades, as the former flow more easily and hence cause less wear and tear of the dies. It is also advisable to do as much of the work as possible in preliminary shaping dies. The steel may also be swaged without any unusual danger of causing the centre to split and it may be upended, providing this process is not carried too far in one operation without reheating. Laps should be carefully avoided, as cracks may start from them when the stampings harden subsequently on air cooling. The fash should be cleaned off stampings whilst they are hot; should they have been allowed to cool without this having been done, they should be reheated to a low red heat and the fash then cleaned off. If these precautions are not carried out, cracks are very likely to form along the fash; thus many table knives are cracked on the heel and bolster because this effect of the fash is not realised.

Finished stampings or forgings should not be thrown

on to damp floors or in places where considerable variations in cooling rate may occur. If the forgings are of simple form, they may be cooled out of draughts and preferably in a warm place. When cold, they will be more or less hard, depending on the composition and may require annealing or tempering before any machining can be done on them. Forgings of intricate pattern, especially those made of the harder varieties of stainless steel, should preferably be charged after final forging, into a furnace at 600° to 700° C. and annealed as described on page 61.

Although the forging or rolling of stainless material which has been heated to ordinary forging temperatures ($1,000^{\circ}$ to $1,200^{\circ}$ C.) should not be continued below 850° to 900° C., owing to danger of cracking, it is practicable to work small sections from an initial temperature of 700° to 750° C., i.e., below the Ac.1 change point. When thus heated, stainless material flows without any danger of cracking, but requires very heavy pressure so that probably few mills or forging appliances are powerful enough to deal with bars finishing greater than about a square inch in cross section. After being worked in this manner, the material may be air cooled without danger, because it will be soft when cold due to the initial reheating temperature being below Ac.1. Bars so rolled or forged have a very fine surface; this is particularly the case if the billet, from which the bar or article is to be rolled or forged, is pickled free from scale before it is reheated for the final rolling or forging operation. The subsequent heating to 700° to 750° C. produces only a very thin film of oxide on the surface and hence the final surface has only an exceedingly thin scale, easily removable by a very short pickling operation. The whole process is somewhat in the nature of cold working in that the crystals of the material are distinctly elongated in the worked bar and the tensile strength of the latter is raised somewhat by the process. Moreover, bars rolled in this way have a very high impact value. In order that the operation may be successful, the temperature of the material must be carefully controlled, since if the limits given above are exceeded the material may prove defective. For this reason the process is likely to be of greater value to the steelmaker who wishes to produce small bars or strip or sheet, and has every facility for controlling temperatures and the necessary technical staff

for supervising the process, rather than to the general user of stainless material. When the necessary control is available, however, the process is exceedingly useful. For example, the heading of small bolts could be carried out by this means and if the bar stock had been previously hardened and tempered to give the required tonnage, no further heat treatment operation would be necessary on the headed bolt. Although the method of low temperature rolling may be used with all grades of stainless material, it is particularly applicable to stainless iron owing to the greater softness of this grade at the rolling temperature. In addition, when this grade has a high chromium content, e.g., 14 or 16 per cent., the rolling temperature may be increased to 800° C. with safety because in such material the Ac.1 change occurs at a higher temperature than in the ordinary types of stainless steel. It may be added that for all such low temperature rolling or forging operations, perfectly sound material is necessary. For example, bars rolled in this way from billets prepared from piped or blown ingots are very liable to split longitudinally during the rolling operation. Those who wish to use the process at all should take care, therefore, that they obtain perfectly sound material such as can only be ensured by skill and care in the melting and casting operations as well as in the subsequent rolling or forging of the ingot.

Small surface defects, such as seams, roaks or laps are always a source of danger during the working or treatment of any steel which hardens intensively, owing to their liability to act as the starting points of cracks. Similarly, material which has to be drop stamped, especially if the latter involves an upending operation, should be free from surface defects, otherwise these may easily extend. All classes of stainless material, except the very mildest, come in the first category, while the milder varieties are especially suitable for drop stamping. In addition to this, perfect freedom from surface defects is essential in any stainless material if its best resistance to corrosion is to be obtained. From such considerations, it is obvious that a perfectly sound surface is a *sine qua non* for all finished products of stainless material.

Ingots of stainless material of reasonable size, e.g., 12 or 14 inches square, can be made under careful supervision with a very good surface. Even with the greatest care,

however, the surface is liable to contain small cavities or irregularities which, on rolling or forging, lead to seams and roaks. For this reason, stainless ingots which are intended for the production of billets for drop stampers or for bars or forgings on which little or no machining will subsequently be done, are almost invariably forged or rolled into blooms the surfaces of which are examined most carefully for defects; these, if found, are removed by machining. The extra cost involved in such examination and machining is worth while both from the point of view of the steel maker who wishes to supply a perfect product and also of the user who is thereby much less likely to have defective or unsatisfactory articles on his hands.

The dangers of seamy bars or forgings cracking badly during heat treatment operations are well known to users of alloy steels which harden intensively. Stainless steel is no exception to the rule and one cannot too strongly emphasise the danger of heat treating or using seamy material without first machining the defects out. In the case of the mildest stainless irons, which do not harden to any great extent, this is not so important but in all the other grades which harden to a Brinell hardness number of about 350 or over, the necessity of this precaution should always be kept in view.

Pickling. The pickling of stainless steel can be carried out quite successfully if certain precautions are observed. If the steel is pickled in the ordinary sulphuric or hydrochloric acid bath it will be found that there is a tendency for the scale to come off in patches only and that if the articles are left in the bath for a longer time in order to remove the rest of the scale, the acid attacks the steel in the places where the scale has already come off, pitting it badly, while the scale remaining on is hardly affected. This is particularly liable to occur if the scale is fairly thick. This undesirable state of affairs, however, can be avoided if a small amount of colloidal organic matter, such as one of the "Restrainers" on the market, is added to the bath. With such an addition, the ordinary pickling bath containing about 5 to 10 per cent. of sulphuric acid acts very well.* The surface

* A suitable restrainer may be made by mixing one part of glue size with one part of concentrated sulphuric acid and then immediately adding, with constant stirring, two parts of water. The mixture, of course, becomes hot (which, it may be remarked, facilitates the reaction between the acid and the glue size), and is ready for use as soon as cold. With a bath containing 5 per cent. sulphuric acid and used at a temperature of 60° to 70° C, the restrainer may be added in the proportion of 1 part to 100 parts of the bath.

produced by such a pickling bath has a tendency to be rather dull in appearance ; it may be brightened up considerably by placing the pickled article for a short period in a cold bath containing about 5 per cent. nitric acid. This bath has only a very slight action on the steel but it has the effect of improving considerably the appearance of the pickled article.

Where a very good surface after pickling is desirable, use may be made of a pickling bath containing 3 to 5 per cent. nitric acid and 1 per cent. of hydrochloric acid. This bath should be used cold ; it works rather slowly but produces a silvery grey surface. The time required varies, with the thickness of the scale, from about half-an-hour or an hour for a very thin coating to about twenty-four hours for a thick scale. This bath will probably be most useful where thin scale, such as is produced by tempering, has to be removed ; for example, in making pressings of stainless iron and steel it may be necessary to do the cold work in several stages and to soften the material between these. For the softening operation, reheating to $700^{\circ}/750^{\circ}$ C. is all that is necessary. Such a reheating produces only a thin film on the surface ; this film can be quickly removed by the special pickling bath, leaving a bright silvery surface in perfect condition for further pressing.

Unless there is some special reason to the contrary, stainless steel should not be pickled when in the hardened condition. Hardened material is generally in a greater or less state of internal stress and if pickled in such a condition, is liable to develop surface cracks.

Heat Treatment of Stainless Material. The subject of the heat treatment of stainless steels of all types is large and many-sided, particularly if one takes into account the effects of variations in composition and temperature of treatment on the physical properties obtained. In the present chapter it is intended to deal only in a general manner with the subject, leaving the detailed consideration of factors such as those mentioned above to the next chapter.

Unless the special precautions mentioned earlier in this chapter are fully carried out, stainless steel, which has been forged or rolled at the ordinary temperatures for such operations, is more or less hard when cold and therefore requires to be softened before any machining or chipping

operations can be carried out. The treatment for such a softening process is very simple; the material merely requires to be reheated to $700^{\circ}/750^{\circ}$ C. and allowed to cool in air, or if preferred it may be quenched in oil or water. After this operation, the material will have a Brinell hardness number of 150 to 250 (corresponding to a tensile strength of 35 to 55 tons per square inch) depending on the amount of carbon it contains and in this condition it machines easily. The operation is simply that of tempering the steel at the highest possible temperature consistent with commercial conditions. A still greater degree of softness, more particularly with the higher carbon varieties, can be obtained by annealing the material, though in this condition, like all annealed steel, it does not machine so smoothly as in the hardened and tempered condition, but is much more liable to tear.

For the annealing process, for reasons which will be evident from Chapter II (page 35), the steel should be heated to 50° or so above the Ac.1 change point (i.e., to $850^{\circ}/880^{\circ}$ C.) and, after allowing to become evenly heated, should be either cooled slowly through the Ar.1 change (e.g., down to 600° C.) or else transferred to a second furnace kept at 600° to 700° C. and, after becoming even, allowed to soak for a sufficiently long period at this temperature to enable the carbon change to take place completely, as described earlier in this chapter. In this case as full annealing, i.e., the production of very soft material rather than the prevention of cracking is the object in view, the soaking time should be generous. Unless the steel is abnormal in composition (e.g., contains considerably more nickel than usual) a soaking period of one or two hours should be ample, after which the material may be air cooled or quenched. In the same way, if the material is slowly cooled in the furnace, the rate of cooling from about 750° to 600° C. should not be faster than 50° an hour. There is no need to continue the slow cooling below 600° C. By such an annealing process, the Brinell hardness number of steel containing 0.30 to 0.40 per cent. carbon may be reduced to between 170 and 200.

All material, whether it has been fully annealed for machining or other purposes or is still in the more or less hardened condition as result of the forging or rolling operations, requires final heat treatment in order to give the best

combination of strength, ductility and toughness for the purpose in view and incidentally to develop its greatest degree of resistance to corrosion. Experience has shown that with all types of steel, and particularly with alloy steels, the best combinations of strength, ductility and toughness are obtained by first hardening the steel so as to produce a homogeneous structure of martensite and then softening the hardened material by tempering so that the required tensile strength or hardness is obtained. In other words, what is aimed at, though possibly unconsciously, is the production of a structure in which there are no sharply defined constituents such as the pearlite and free ferrite or cementite which are obtained by normalising ordinary carbon steels and such alloy steels as do not air harden or by annealing practically all steels; but, rather, a structure in which the carbide occurs in minute granules evenly distributed in a background of fine grained ferrite. Actually, much of the superiority of alloy steels is due to the fact that they can be completely hardened with ease in bars or pieces of a size which by no practicable method of quenching could be hardened throughout if made of ordinary carbon steel. Such hardened bars of alloy steel may then be tempered and, as a result, have a high degree of uniformity of hardness, toughness and ductility from surface to centre. These good features are possessed by stainless steel in common with other alloy steels which air harden or oil harden with ease.

To harden stainless steel, it should be heated to a temperature which is, in general, in the range 900° to 950° C., and then be cooled in air or quenched in oil or water, depending on circumstances. If the cross section of the piece is reasonably small and only a moderate degree of hardness is required, air cooling is generally satisfactory. When a greater degree of hardness is required or if the cross section of the piece is large, then oil quenching may be used. Water quenching is permissible if the section is symmetrical and able to withstand great stresses, or if practicable and convenient as in the case, for example, of knife blades. With stainless iron the hardening capacity depends on the chromium content. Material with about 10 to 14 per cent. chromium and 0.07 to 0.10 per cent. carbon will oil harden, or air harden in reasonably small sections, from a temperature of 950° C.

to a Brinell hardness number of 250 to 350. With a higher content of chromium than this, however, the hardening capacity falls off considerably (as indicated in Fig. 50, page 91), so that at about 16 per cent. chromium one cannot obtain a Brinell hardness of more than about 250, even by water quenching small samples, while the maximum hardness obtainable by air cooling is less than this.

Where articles of complex shape have to be dealt with, especially if the carbon content is fairly high, air hardening is preferable to oil hardening, in order to minimise quenching stresses. If, at the same time, the cross section of the article is fairly great in parts, so that the rate of cooling of such parts is hardly fast enough to harden them sufficiently, advantage may be taken of the fact that the capacity of the steel for air hardening increases as the hardening temperature rises. For such purposes a temperature of 950° to 975° C. may be used or even $1,000^{\circ}$ C. It is not advisable to exceed the latter temperature, however, as by so doing a coarse structure is liable to be produced. Where such difficulties arise in the production of sufficient hardness by air cooling, and oil quenching is not advisable, matters may be helped considerably by using a steel containing one per cent. or thereabouts of nickel, since the presence of this element greatly retards the rate at which the critical changes take place on cooling and hence allows the material to harden at slower rates of cooling (see page 124).

As a general rule, the tempering operation should follow the hardening as soon as possible, in order that stresses set up in hardening may be relieved before they have an opportunity to cause cracking. This, of course, applies equally to all steels which harden intensively. There is no need to wait until the article is quite cold after hardening. The lowered change point which results in the production of martensite from austenite takes place between 250° and 400° C. (see page 53) depending on composition and hardening temperature and as soon as this change has taken place completely, the article may be reheated for tempering. As the steel becomes strongly magnetic when the above change takes place, a magnet may be used as a guide.*

Articles which are to be retained in the hard condition should preferably be tempered between 200° and 400° C.

* See p. 61 with respect to stainless iron, however.

after hardening. By so doing, quenching stresses are relieved and the toughness improved distinctly. It has been shown earlier (Fig. 13) that such tempering has practically no effect on the hardness. Owing to this resistance to tempering, it is possible to combine the hardening and tempering operations by quenching the material from the hardening temperature in a fused salt or metal bath, the temperature of which is kept between 150° and 250° C. Such a method is valuable for articles which are liable to crack when quenched in the ordinary way. It is important to note that the temperature of the bath should not be allowed to rise above the range indicated above. The upper limit is fixed by the fact that the temperature must be lower than that of the lowered change point, otherwise the material is retained in the austenitic condition whilst in the bath, and fully hardens on cooling from the latter.

Some little difficulty may be experienced in properly refining stainless steel which has been badly overheated, especially if, after such overheating, it has been allowed to cool slowly, producing a pearlitic structure. This is especially the case if the carbon exceeds about 0.3 per cent. The cause of this will be evident from the description of the microstructure given in Chapter II. Material which has been slowly cooled from a high temperature consists of pearlite and frequently, as shown in Fig. 8, the distribution of the carbide in such pearlite is not by any means uniform even when the steel is of eutectoid composition. With lower carbon than this, the distribution of carbide is still more irregular owing to the presence of ferrite (see Figs. 3 and 21). When such material is reheated to $900^{\circ}/950^{\circ}$ C. for hardening, the ground mass of austenite formed at A_{c1} is, of course, refined, but the carbide which remains undissolved at these temperatures (see Figs. 10 and 23) still outlines the original coarse structure and hence the material, after such hardening, is not properly refined. In the case of steels containing more than 0.3 per cent. carbon (i.e., hyper-eutectoid) the excess carbide which has probably formed a network round the grains of the overheated material, as in Fig. 4, remains quite undissolved at 900° to 950° C., and further aggravates matters. Such cases are dealt with by reheating material containing 0.3 per cent. carbon or less to $975^{\circ}/1,000^{\circ}$ C. or in the case of higher carbon steel, to

a temperature sufficiently high to dissolve the excess carbide (see Fig. 27), and air cooling therefrom, so as to keep the carbide evenly diffused. The articles may then be hardened and tempered in the normal way.

Hardening from such high temperatures as those given above for the preliminary heat treatment is rather prone to lead to cracking, especially if the article has a form which is likely of itself to cause trouble in this respect; it may therefore be necessary to take precautions to avoid this. Such cracking almost invariably occurs either while the article is passing through the lowered change point or afterwards. Where cracking is liable to occur, therefore, the article should be air cooled down to about 450° or 400° C. (in order to prevent the separation of pearlite or troostite at Ar.1) and may then be cooled comparatively slowly through the range in which the lowered transformation occurs. Thus, after it has air cooled down to about 400° C., it may be charged into a furnace at this temperature and allowed to cool slowly in that, or the cooling rate may be retarded by other means such as packing in hot ashes. As in the normal hardening operation, the article may be reheated for the final hardening process as soon as it has passed through the lowered change point and before it becomes cold.

The improvement which is brought about by such a preliminary treatment as that given above may be illustrated by the following tests obtained on two bars ($1\frac{1}{8}$ inches diameter) of steel of the following composition :—

Carbon	0.30	%
Silicon	0.17	%
Manganese	0.23	%
Chromium	12.4	%
Nickel	0.55	%

These bars were soaked for three to four hours at $1,100^{\circ}$ C. and then slowly cooled, so as to produce a very coarse pearlitic structure. After this treatment they had a Brinell hardness number of 202 and an Izod impact figure of 5 foot lbs., the fracture being coarsely crystalline. Bar A was given a refining treatment at $1,000^{\circ}$ C. and was then hardened at 900° C. and tempered at 700° C. in the usual way. Bar B was

hardened at 900° C. and tempered at 700° C., along with A, but was not given the refining treatment. These bars gave the following tests :—

	Yield Point, tons per square inch.	Maximum Stress, tons per square inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Izod Impact, ft. lbs.
A. (refined)	38.2	52.6	25.0	58.2	59 64
B. (not „)	36.8	49.8	22.0	48.5	26 24

The improvement in the microstructure brought about by this refining treatment is typified by a comparison of Fig. 15 with Figs. 9 and 10. The structure of the refined bar was similar to Fig. 15; in the unrefined piece, the plates of the carbide formed a “ghost image” of the original structure, resulting from the annealing operation, in a fashion typified by Figs. 9 and 10. Such plates provide a favourable path on which a crack may readily travel. On the other hand, the structure shown in Fig. 15 is free from all traces of this coarse structure.

Welding, Brazing and Soldering. There is no particular difficulty with regard to the soldering of stainless material. Possibly the ordinary lead-tin solder does not unite with the stainless steel quite so easily as it does with ordinary steel, but there is no difficulty in making a joint. Zinc chloride is a suitable flux.

Stainless steel can be brazed, though with some difficulty, with the ordinary brazing mixtures, using borax as flux. A greater difficulty arises, however, not with the brazing operation itself but with the condition the stainless material assumes after the operation is completed. The ordinary copper-zinc brazing mixture (60 per cent. copper, 40 per cent. zinc) requires the material, which is to be brazed, to be heated to a temperature of at least 950° C. for the operation to be successful. On cooling down from such a temperature, stainless steel hardens to a greater or less degree depending on the carbon content and hence, when a brazed joint is made in such steel, the parts of the latter immediately surrounding the joint will be more or less hard and brittle when the material cools down after the joint is made. This condition can, of course, be rectified by reheating the brazed



FIG. 41. Group of small stainless iron turbine blades oxy-acetylene welded to a mild steel ring. Slightly enlarged.

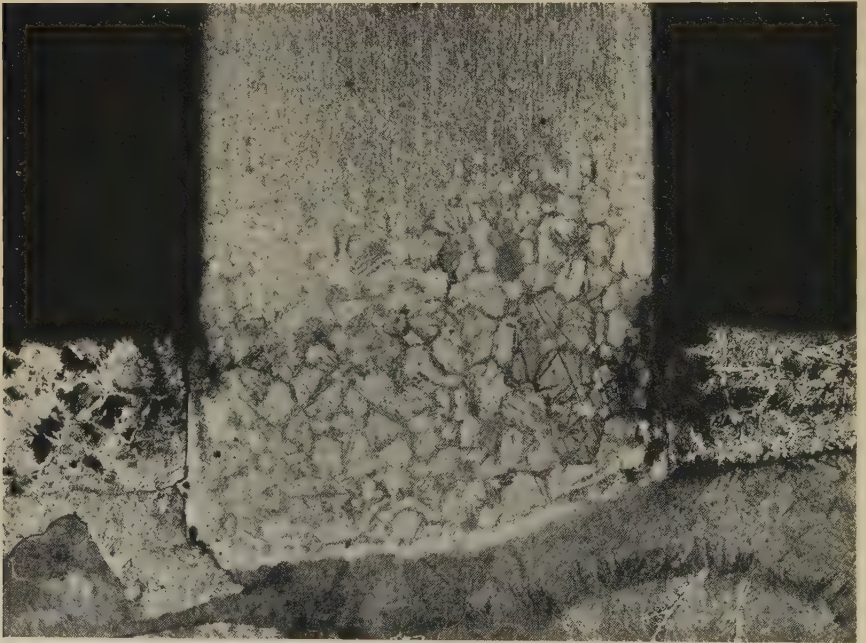


FIG. 42. Section through one of the joints in Fig. 41. $\times 15$.

sample to a temperature of about 700°C. , but in some cases this is not convenient. For example, the blades of a turbine are frequently brazed to shrouding wires which hold them firmly together, preventing an undue amount of flexure. It is generally not feasible to temper the whole of such a disc, after the shrouding wires have been brazed into position, owing to its size and for other reasons. In order, therefore, to minimise the production of hard brittle spots in such blades it is preferable to use a brazing mixture having a considerably lower melting point than the ordinary 60 : 40 brass. It has been found that an alloy having the following composition :—

Copper	44 %
Zinc	33 %
Silver	23 %

is very suitable for this purpose. It melts at a temperature of about 700°C. and hence allows the brazing to be carried out with much less danger of hard brittle spots being formed in the stainless material afterwards. It also forms a very strong joint.

It is also obvious that for purposes involving brazing, it is preferable to use the lower carbon stainless iron than material of higher carbon content, because the former air hardens to a very much less degree than the latter, especially from temperatures not much higher than the Ac.1 point. By using the lower carbon material, the bad effects of an accidental overheating in the brazing operation are very much less marked than they are with the higher carbon steel.

Using the brazing mixture mentioned above, pieces of stainless iron strip, 2 in. wide, $\frac{1}{16}$ in. thick, have been brazed and then, without further treatment, the strip bent through 180° close to the joint without the latter showing any sign of failure or the strip in the neighbourhood showing the least sign of cracking.

Stainless material cannot be welded at the smith's hearth in the same way as ordinary mild steel, but it can be welded quite easily with the electric arc or the oxyacetylene blowpipe. Thus Fig. 41 shows a group of small turbine blades of stainless iron welded (with the oxyacetylene

blowpipe) to a mild steel ring. Fig. 42 shows, at a low magnification, a section through one of the welds and Fig. 45a, at a rather higher magnification, the actual junction between the stainless iron and mild steel. It will be seen that welding has actually taken place; there is no sharp line between the two steels. More care is necessary in oxy-acetylene welding stainless material than ordinary steel, as it is more easily burnt; otherwise, the operations on the two materials are similar.

Stainless material may readily be welded electrically either by the arc, seam or spot methods. Fig. 43 shows a section through a "spot weld" between two stainless iron sheets; here again true welding has undoubtedly been obtained.

As with ordinary carbon steel, welding becomes more difficult as the carbon content of stainless steel increases. When articles of stainless material have to be welded, therefore, it is advisable to use material of as low a carbon content as possible, i.e., stainless iron in preference to stainless steel.

All stainless material which has been welded either electrically or by the oxyacetylene blowpipe will be hardened near the weld to a greater or less extent, depending mainly on the carbon content. Such welded material should therefore be softened by tempering at 600° to 700° C. This can often be done quite readily by the welder himself; e.g., when small pieces are being oxyacetylene welded, the part heated by this operation can be easily tempered by a second application of the blowpipe after the material has cooled down from the welding operation.

When two pieces of stainless material are being welded and the joint itself has to be corrosion resisting, it is, of course, necessary to use welding rods of special material. For arc welding operations the special A.W.P. electrodes supplied by the Alloy Welding Processes, Ltd., are suitable. For oxy-acetylene welding, the firm the author is associated with supplies a special welding material which makes a satisfactory joint. A section through a lap weld, for which this welding rod was used, is shown in Fig. 44; Fig. 45b, taken at a much higher magnification at the actual junction of the sheet and the welding material, indicates, by the fact that the grain boundaries cross this junction, that a very definite union between the metals has taken place.



FIG. 43. Section through spot weld between two stainless iron sheets (10 gauge). $\times 15$. The position of the weld is evident from the unwelded surfaces of the sheets which are visible on either side of the photograph.



FIG. 44. Lap weld (oxy-acetylene) between two pieces of 18-gauge stainless iron sheet. The special stainless welding rod mentioned on page 76 was used for this weld. $\times 18$.

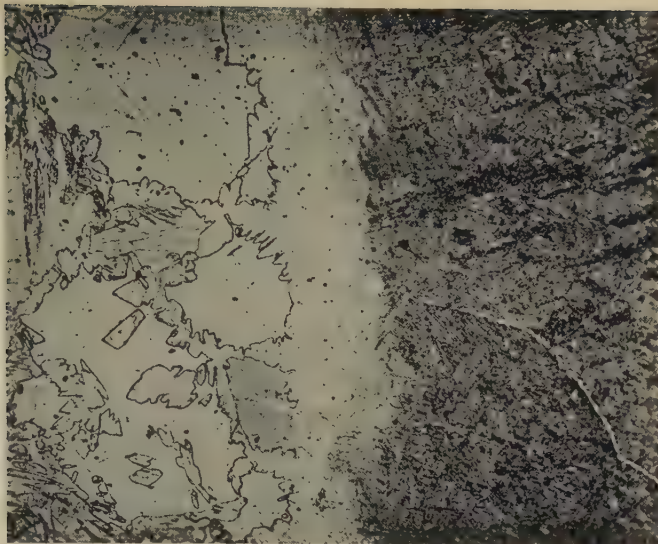


FIG. 45a. Part of the weld shown in Fig. 42, magnified 100 diameters, showing the junction between the stainless iron (left hand) and the mild steel.

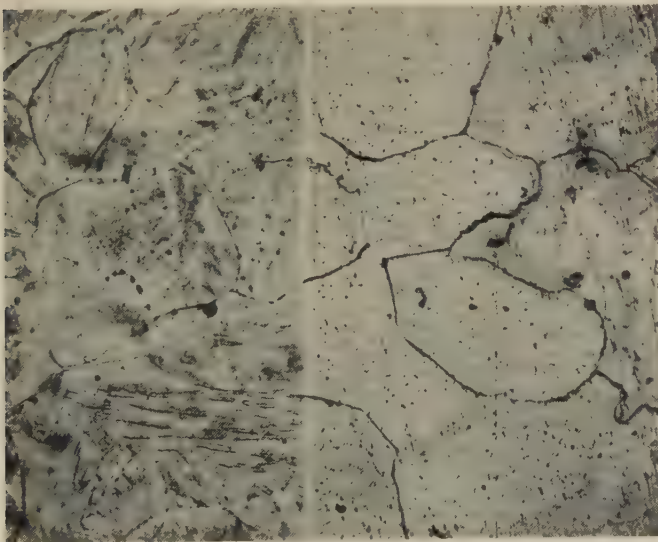


FIG. 45b. Part of the weld shown in Fig. 44, magnified 750 diameters, showing the junction between the stainless iron (left hand) and the welding material. Note the grain boundaries crossing the weld, indicating metallic continuity.

MECHANICAL AND PHYSICAL PROPERTIES OF
STAINLESS STEELS IN RELATION TO
VARYING TREATMENT AND COMPOSITION

CHAPTER IV

MECHANICAL AND PHYSICAL PROPERTIES OF STAINLESS STEELS IN RELATION TO VARYING TREATMENT AND COMPOSITION

There appears to be a very large and promising field for the use of stainless material for engineering work of many types, and as the suitability or otherwise of any material for such purposes is judged to a large extent by its physical properties, as shown by the different types of mechanical tests which are in use for this purpose, it is important that the considerable range of mechanical properties obtainable from stainless material and which fits it for use under very diverse conditions, should be studied in some detail.

As pointed out in the last chapter, experience has shown that with all types of steel, particularly with alloy steels, the best combinations of strength, ductility and toughness are obtained by first hardening the steel so as to obtain a homogeneous structure of martensite and then softening the hardened material by tempering so that the required tensile strength or hardness is obtained. By varying the tempering temperature, a considerable range of mechanical properties may be obtained from any one steel; the extent of this range may be indicated in a very satisfactory and useful manner by suitably hardening a number of bars of the steel and then tempering them at a series of gradually increasing tempering temperatures. The size of the bar chosen for such tests has often a very important bearing on the results obtainable from a given steel. The smaller the diameter of a bar, the more quickly it may be cooled and with a steel such as ordinary carbon steel, in which the rate of cooling necessary to harden the steel is comparatively fast, the amount of hardening obtained depends, in a very great degree, on the size of the bar used. Air hardening steels such as stainless harden at comparatively slow rates of cooling and therefore are not so susceptible to

mass effects; hence the results obtained from such steels by using bars of small size, for example, one inch or so in diameter, can be applied to bars of considerably larger size. Most of the tests given in this chapter were obtained on bars one inch to one-and-a-quarter inches diameter, but the results may be applied, with some limitations to be dealt with later, to bars five or six times that size.

The results obtainable from stainless iron after oil hardening and then tempering at various temperatures are illustrated in Table I, which gives the tests obtained from material containing : —

Carbon	...	0·07 %
Silicon	...	0·08 %
Manganese	...	0·12 %
Chromium	...	11·7 %
Nickel	...	0·57 %

These results are plotted in Fig. 46, which enables the variation of mechanical properties with tempering temperature to be visualised more readily.

For such very mild material as this, quenching in oil is sometimes preferable to air hardening, because the hardness obtained by air cooling is, generally speaking, somewhat lower than that by quenching in oil. The difference is probably due, not to the breakdown of the martensite during air cooling, but to the separation of ferrite, the latter being hindered by the more rapid cooling in oil. From the heat treated bars tensile test pieces were machined (British standard size, 2 in. by 0·564 in.) and also test pieces for the Izod impact test (10 mm. square test pieces, standard "Vee" notch), the latter test indicating the toughness of the material and being, in the author's opinion, of the greatest importance in judging the quality of steel for engineering purposes.

The bars, when hardened, had a tensile strength of approximately 73 tons per square inch, and in this condition possessed good ductility and toughness. The effect of tempering on the tensile strength was such as would be expected from the Brinell hardness curves given in Fig. 13. Up to a temperature of 500° C. the tensile strength was practically unaffected by tempering while the toughness and ductility were notably improved. Between 500° and 600° C.

TABLE I.
Mechanical Properties of Stainless Iron.
 (Bars treated : $1\frac{1}{8}$ " diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0.07	0.08	0.12	11.7	0.57

Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
*O.H. 930° C. ...	—	73.2	13.5	41.9	340	28
„ W.Q. 200° C. ...	—	73.0	12.0	38.0	340	34
„ „ 300° C. ...	—	72.4	12.5	36.4	332	38
„ „ 400° C. ...	—	72.3	15.5	51.0	332	38
„ „ 500° C. ...	58.8	72.4	18.0	52.2	340	36
„ „ 600° C. ...	38.0	49.1	22.0	62.4	241	65
„ „ 700° C. ...	30.6	40.4	26.5	65.8	196	79
„ „ 750° C. ...	27.9	36.4	31.0	68.8	179	87
„ „ 800° C. ...	33.6	53.6	13.5	44.6	255	40

the tensile strength fell rapidly so that the bars tempered at the latter temperature gave a figure of 49 tons per square inch. Concurrently with this fall in tensile strength, there was a distinct increase in the ductility figures (elongation and reduction of area) and a still more marked increase in the toughness value. As the tempering temperature rose from 600° to 750° C., the tensile strength fell steadily from 49 tons per square inch to just under 37 tons per square inch, the ductility figures at the same time increasing regularly. In this steel, the carbon change point occurred between 790° and 800° C., and hence the bar tempered at 800° C. showed distinct hardening effects which were made more evident owing to the bars being quenched in water from the tempering heats.

* In the preparation of tables, the use of readily understandable abbreviations is often a matter of some convenience. The signs W.H., O.H., A.H., are easily apparent abbreviations for water, oil, and air hardening, respectively. With regard to tempering temperatures, it will be shown later that the speed of cooling after a tempering operation may have a distinct influence on the impact results obtained from a treated test piece. Test pieces are therefore generally quenched in water from the tempering heat and the expression W.Q. 600°C. indicates that a sample was so quenched from this tempering temperature. Similarly F.C. 600° C. and A.C. 600° C. indicate respectively cooling more or less slowly in a furnace and air cooling from the tempering heat.

It may be of interest to note that the results given above were obtained from the first cast of stainless iron produced on a commercial scale and which was referred to on page 14.

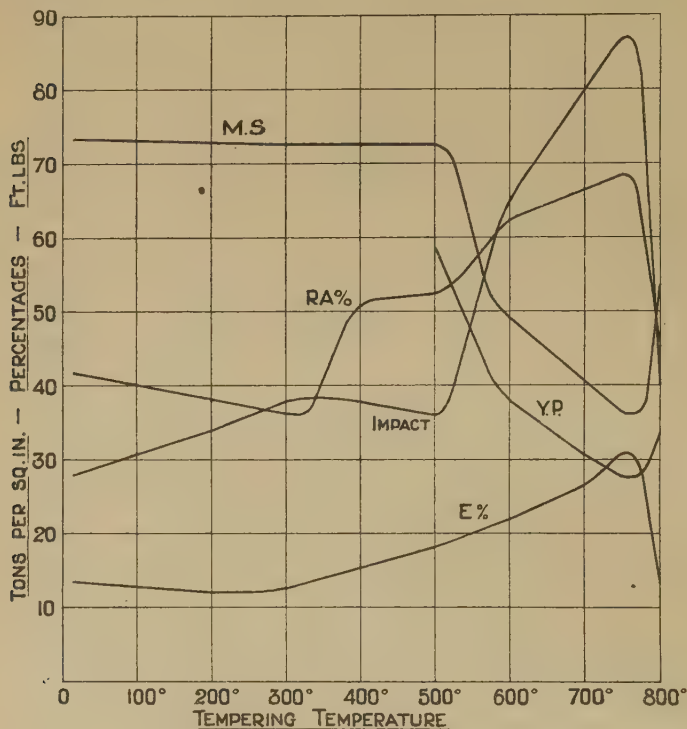


FIG. 46. Mechanical properties of stainless iron, containing 0.07 per cent. carbon and 11.7 per cent. chromium, after hardening and tempering.

Results similarly obtained on a sample with somewhat higher carbon and having the following analysis —

Carbon	0.10%
Silicon	0.46%
Manganese	0.31%
Chromium	11.2 %
Nickel...	0.44%

are given in Table II and plotted in Fig. 47. In this case the material when hardened had a tensile strength of 85 tons per square inch, and after fully tempering, at 750° to 800° C., a value of about 40 tons per square inch was obtained.

A test after air hardening is also given and illustrates the somewhat lower tonnage obtained by air cooling as compared with oil quenching. In many cases, however, and especially if the bars are afterwards fully tempered, the difference between air hardened and oil hardened bars is negligible.

TABLE II
Mechanical Properties of Stainless Iron.
(Bars treated: $1\frac{1}{8}$ " diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0.10	0.46	0.31	11.2	0.44

Treatment.		Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduction of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.		
A.H. 950° C.	69.2	78.0	12.0	36.4	302	18	20	20
O.H. 950° C.	—	84.7	3.0	8.4	340	20	31	28
„	W.Q. 500° C.	—	82.6	18.5	57.0	340	19	18	18
„	„ 600° C.	46.0	55.0	22.0	63.7	241	24	29	
„	„ 700° C.	36.0	43.6	27.0	66.8	192	120	120	120
„	„ 750° C.	32.7	40.8	32.0	67.0	179	120	120	120
„	„ 800° C.	28.8	39.6	32.5	65.8	170	109	110	105

With increasing carbon content in the steel, similar types of curves to those in Figs. 46 and 47 are obtained. The values of the tensile strength of such samples, under given conditions of heat treatment, gradually rise while the toughness and ductility figures become less. Steels with carbon content between 0.15 and 0.25 per cent. are very well adapted for many engineering purposes where a somewhat higher tensile strength than that given by stainless iron is required. Thus Table III and Fig. 48 give the test figures obtained from a steel containing

Carbon	...	0.22 %
Silicon	...	0.11 %
Manganese	...	0.17 %
Chromium	...	11.5 %
Nickel	...	0.76 %

and illustrate the useful combinations of tensile strength and toughness which such a steel will give. At the same

time, when hardened, followed or not by tempering up to $500^{\circ}\text{C}.$, it is sufficiently hard (Brinell hardness number 400 to 450) to serve for many purposes where a surface to resist erosion or wear is required.

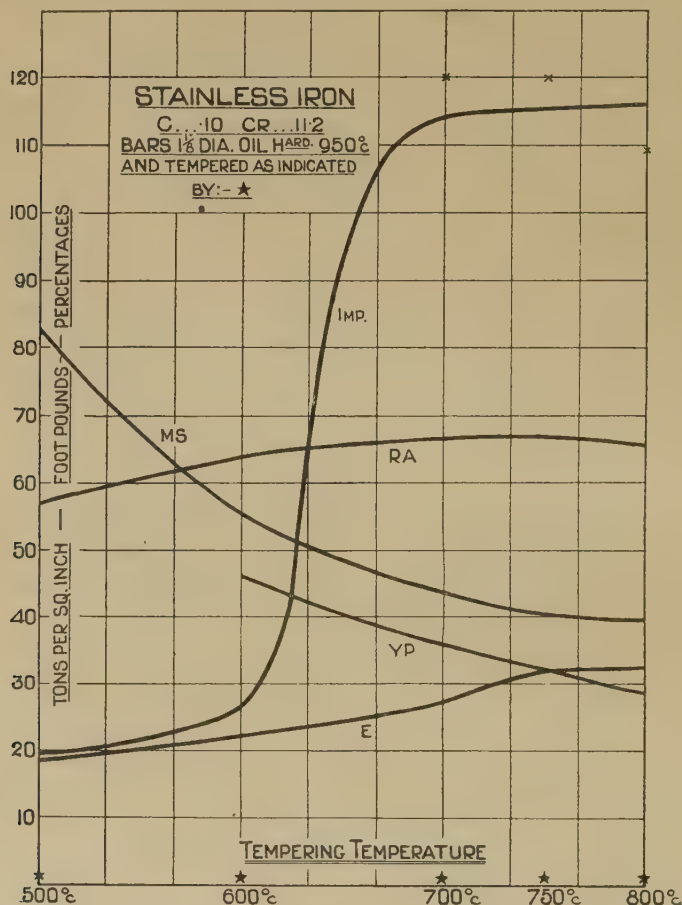


FIG. 47. Mechanical properties of stainless iron, containing 0.10 per cent. carbon and 11.2 per cent. chromium, after hardening and tempering.

When the carbon content rises over about 0.30 per cent., the steel becomes hypereutectoid and hence more in the nature of a tool steel than a constructional steel. Such steels when hardened give higher Brinell hardness numbers than those with lower carbon and they cannot be softened by tempering below a tensile strength of 50 to 55 tons per square inch. Increase in carbon content in this range has not such a noticeable effect on the mechanical properties obtainable under

TABLE III.
Mechanical Properties of Mild Stainless Steel.
(Bars treated : 1 $\frac{1}{8}$ " diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0.22	0.11	0.17	11.5	0.76

Treatment.		Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Izod Impact, ft. lbs.
O.H. 900° C.	W.Q. 500° C. ...	84.4	88.0	9.5	36.4	15 14 18
"	" 600° C. ...	42.0	56.4	24.0	52.2	25 23
"	" 700° C. ...	38.0	46.8	26.0	58.0	60 60 67
"	" 750° C. ...	31.2	43.9	28.0	61.5	68 63 70

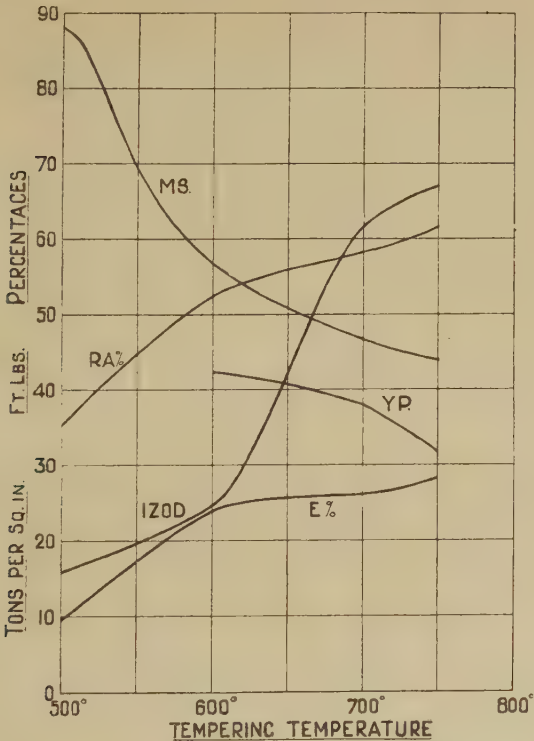


FIG. 48. Mechanical properties of stainless steel, containing 0.22 per cent. carbon and 11.5 per cent. chromium, after hardening and tempering.

given conditions of treatment as it has in the lower ranges of carbon. This is illustrated by the results given in Tables IV and V, which refer to steels containing 0.37 and 0.50 per cent. carbon respectively and which also show that such steels when properly treated are quite tough and ductile.

TABLE IV.
Mechanical Properties of Hard Stainless Steel.
(Bars treated: $1\frac{1}{8}$ " diameter.)

	Carbon %	Silicon %	Manganese %	Chromium %			
	0.37	0.19	0.15	11.7			
Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.	
A.H. 900° C. ...	—	102.0	3.0	3.24	444	5	3 3
„ W.Q. 300° C.	—	100.0	5.5	6.7	444	5	5 5
„ „ 500° C.	—	104.4	9.0	24.6	444	8	4
„ „ 550° C.	—	91.2	9.0	30.6	437	11	11 7
„ „ 600° C.	57.8	65.0	11.5	27.6	302	7	10 7
„ „ 650° C.	50.2	56.4	17.5	37.8	269	15	10 15
„ „ 700° C.	46.8	54.0	21.0	52.2	241	26	26 21
„ „ 750° C.	42.4	51.8	21.0	44.6	241	28	33 34

TABLE V.
Mechanical Properties of Hard Stainless Steel.
(Bars treated: $1\frac{1}{8}$ " diameter.)

	Carbon %	Silicon %	Manganese %	Chromium %			
	0.50	0.14	0.13	12.2			
Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.	
A.H. 900° C. ...	—	—	—	—	477	4	5 4
„ „ W.Q. 300° C.	—	—	—	—	444	6	4 5
„ „ „ 400° C.	—	103.2	7.5	11.8	444	6	5 6
„ „ „ 500° C.	—	93.2	6.0	21.4	415	3	3 4
„ „ „ 600° C.	55.6	62.0	15.0	42.0	285	13	13 14
„ „ „ 650° C.	50.2	56.8	18.0	45.9	262	12	12 13
„ „ „ 700° C.	46.4	53.6	20.0	49.7	241	24	25 25
„ „ „ 750° C.	42.6	51.4	28.0	52.2	245	30	30 30

With a still higher carbon content than this, the material contains very large amounts of free carbide ; as an indication however, of the type of mechanical properties obtainable from such steels, the results given in Table VI are included. They are interesting also in that they confirm what was said above, that the effect of increasing carbon content on the mechanical properties of these high carbon steels, under given conditions of heat treatment, is not nearly so marked as it is with steels of lower carbon content.

TABLE VI.
Mechanical Properties of High Carbon Steels.

ANALYSIS.

No.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
1	0.96	0.17	0.33	13.1	0.45
2	1.08	0.17	0.34	13.1	0.50
3	1.18	0.10	0.29	13.1	0.45
4	1.42	0.12	0.35	13.1	0.44

TESTS (Bars treated : $1\frac{1}{4}$ " diameter.)

No.	Treatment.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
1	A.H. 900° C. W.Q. 650° C.	30.0	59.0	10.0	18.3	265	9 8 8
	" " 700° C.	35.6	53.8	18.5	36.4	255	7 7 10
	" " 750° C.	41.2	53.5	19.0	39.2	241	14 13 17
2	A.H. 900° C. W.Q. 650° C.	44.4	62.4	7.0	10.1	285	11 9 22
	" " 700° C.	38.0	56.6	17.5	29.1	277	17 16 21
	" " 750° C.	44.0	57.8	14.5	29.1	265	13 9 15
3	A.H. 900° C. W.Q. 650° C.	40.8	61.6	8.0	11.8	285	15 17
	" " 700° C.	40.8	58.2	15.5	30.6	277	17 11
	" " 750° C.	30.0	56.8	15.0	26.1	265	15 10 16
4	A.H. 900° C. W.Q. 650° C.	38.0	61.9	7.0	13.4	302	11 5 5
	" " 700° C.	40.8	59.7	10.0	18.3	385	8 8
	" " 750° C.	33.6	58.9	10.0	18.3	281	5 14 5

Hardening Temperature. It will be noticed from the diagrams and figures given that the hardening temperature required for stainless steels varies somewhat with the carbon

content of the material to be treated. For the mildest steels or stainless irons, and also those of somewhat higher carbon content, i.e., 0.15 to 0.20 per cent, air cooling or oil quenching from 950° C. provides a suitable method. At about 0.25 per cent. carbon, the temperature may with advantage be dropped to 925° C. while for 0.3 per cent. carbon and upwards 900° C. forms an efficient hardening temperature. The effect of varying hardening temperature on the resistance to corrosion will be dealt with in a later chapter but the effect on the mechanical properties of increasing the hardening temperature may be briefly dealt with here.

In Chapter II, the progressive solution of the carbide in the steel, as the latter is heated through the range of a hundred and fifty degrees or so above the Ac.1 point, was described, and also its effect on the hardness of samples quenched in this range. Owing probably to this gradual solution of the carbide, the air hardening capacity of the steel also increases as the temperature, from which air cooling takes place, rises through the same range. The solution of the additional carbide appears also to increase the tensile strength of the steel after tempering at a given temperature so that if bars of the same steel are hardened, for example, at 900°, 950°, and 1,000° C., not only would the samples hardened at the higher temperatures be somewhat harder than those hardened at the lower temperatures (and also, incidentally, would harden at slower rates of cooling) but in addition, if the samples so treated were tempered together at, for example, 700° C., the one hardened at 900° C. would have the lowest and that hardened at 1,000° C. the highest hardness and tensile strength. The greater hardness obtained, after tempering, from samples quenched at higher temperatures was noted in connection with high carbon steel (page 45, and Fig. 33) and is also illustrated by the curves in Fig. 49, in which are plotted the Brinell hardness numbers obtained from samples of a steel containing

Carbon	0.32	%
Silicon	0.26	%
Manganese	0.29	%
Chromium	12.2	%
Nickel	0.85	%

which had been oil quenched from 900° and 1,050° C. respectively. In all cases, the samples quenched at high and

low temperatures were tempered together in the same furnace. It will be seen that the hardness of the samples quenched from the higher temperature remains steadily above that of the other samples until the tempering temperature reaches the Ac.1 point.

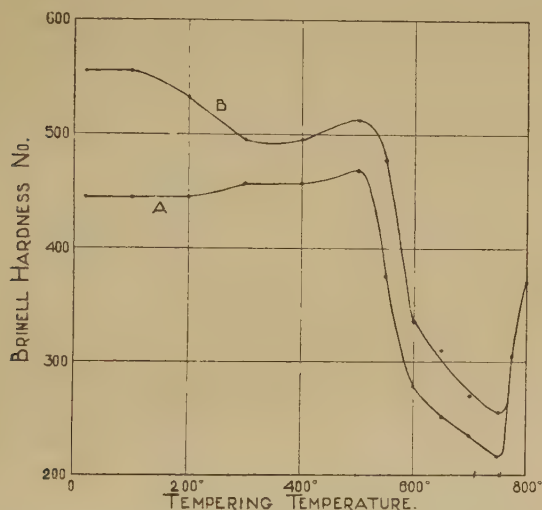


FIG. 49. Effect of hardening temperature on the subsequent tempering of stainless steel (0.32 per cent. carbon and 12.2 per cent. chromium).

Curve A. Hardened at 900°C.

Curve B. „ „ 1,050°C.

The influence of the hardening temperature on the mechanical properties is also illustrated by the figures given in Table VII, which show, in addition, that the increased hardness produced by the higher quenching temperature is accompanied by a notable decrease in toughness. This, of course, is in line with what occurs with other types of steel.

Similar results are obtainable from even the low carbon stainless irons, though in this case, the drop in toughness may not be so noticeable. It is quite perceptible, however, with a steel containing 0.16 per cent. carbon as will be seen from the figures given in Table VIII.

High Chromium Irons and Steels. The data given in the preceding pages apply to material containing the normal amounts of chromium found in stainless material, namely 11 to 14 per cent. If the upper limit is exceeded to

any great extent, the properties of the material change in certain directions, the most important of these changes being in respect of the hardening capacity of the material. As the chromium increases above 14 per cent., a higher quenching temperature is necessary to harden the steel, as would be

TABLE VII.

Effect of Hardening Temperature on Hardness and Toughness of Stainless Steel.

(Bars treated: $1\frac{1}{8}$ " diameter.)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0.25	0.18	0.22	12.5	0.21

Treatment.	Brinell Hardness No.		Calculated Tensile Strength. Tons per sq. in.	Izod Impact, ft. lbs.
	After Hardening.	After Tempering.		
A.H. 900° C. W.Q. 700° C.	430	228	50	85 86 80
A.H. 950° C. ,,	477	241	52	47 67 71
A.H. 1,000° C. ,,	532	248	54	36 35 35

TABLE VIII.

Effect of Hardening Temperature on the Hardness and Toughness of Mild Stainless Steel.

(Bar treated: $1\frac{1}{8}$ " diameter)

Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
0.16	0.52	0.27	13.0	0.31

Treatment	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elonga- tion % on 2 ins	Reduc- tion of Area %	Brinell Hardness No.		Izod Impact, ft. lbs.		
					Hard'd.	Temp'd			
O.H. 900° W.Q. 750° C.	34.0	44.2	33.0	67.8	336	196	110	111	110
O.H. 950° ,,	40.8	47.8	28.0	65.8	402	217	95	108	93
O.H. 1,000° ,,	42.0	49.1	25.0	63.6	444	235	82	93	95

expected from the general effect of chromium in raising the critical ranges of the material and retarding the solution of the carbide; at the same time, the capability of the material for hardening diminishes very markedly so that eventually the increase in hardness obtainable by quenching from any temperature up to at least $1,200^{\circ}\text{C.}$, becomes very small. The effect of any given content of chromium varies with the

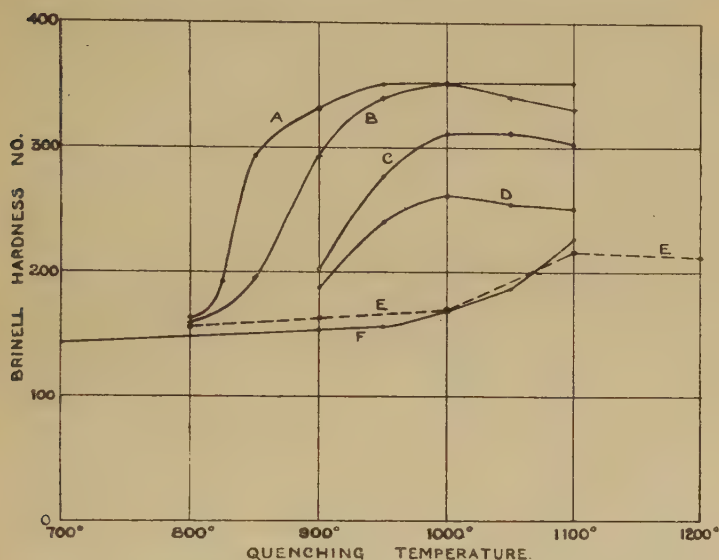


FIG. 50. Effect of chromium content on the hardness obtained by water quenching low carbon steels from various temperatures:—

Curve.	Carbon %.	Chromium %.
A.	0.07	11.5
B.	0.08	14.0
C.	0.09	15.0
D.	0.07	16.0
E.	0.12	18.8
F.	0.10	20.4

carbon content of the material, the lower carbon irons losing their hardening capacity with a lower chromium content than the higher carbon steels. The effect may be illustrated by the curves given in Figs. 50 and 51, which show the Brinell hardness numbers obtained on water quenching steels containing varying amounts of carbon and chromium from different temperatures. The samples used for the quenching tests were short pieces, $1\frac{1}{2}$ -in. to 2-in. long, cut

from bars, $\frac{1}{2}$ -in. to $\frac{9}{16}$ in. square. The curves in Fig. 50 relate to low carbon steels having the following analyses : —

Curve	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0.07	0.14	0.13	11.5	0.39
B.	0.08	0.23	0.18	14.0	0.31
C.	0.09	0.35	0.14	15.0	0.28
D.	0.07	0.25	0.14	16.0	0.34
E.	0.12	0.15	0.24	18.8	0.26
F.	0.10	0.31	0.10	20.4	0.30

The iron containing 14 per cent. chromium requires a higher temperature for hardening than that with 11.5 per cent., but eventually reaches the same hardness as the latter. When the chromium exceeds 14 per cent., however, the falling off in the hardening capacity of such low carbon steel is very marked and is brought out clearly in the diagram.

In. Fig. 51, the results obtained from steel of higher carbon content are plotted. Those marked G and H, having the following analyses :—

Curve	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
G.	0.17	0.26	0.18	15.9	0.31
H.	0.17	0.21	0.18	17.1	0.27

may be compared with D and E in Fig. 50, when the influence of the higher carbon will be evident.

The remaining samples, the results on which are plotted in Fig. 51, had the following analyses :—

Curve	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
J.	0.48	1.06	0.35	15.1	1.37
K.	0.53	0.22	0.29	16.8	—
L.	0.87	0.72	0.25	17.6	0.19
M.	0.42	0.78	0.32	25.0	0.48
N.	1.9	0.91	0.27	27.5	0.36

The first three of these show that material containing the high chromium percentages indicated will harden quite satisfactorily if it has a carbon content distinctly higher than that found in ordinary stainless steel. The fall in hardness obtained on quenching these steels at 1,200° C. is due to the production of austenite.

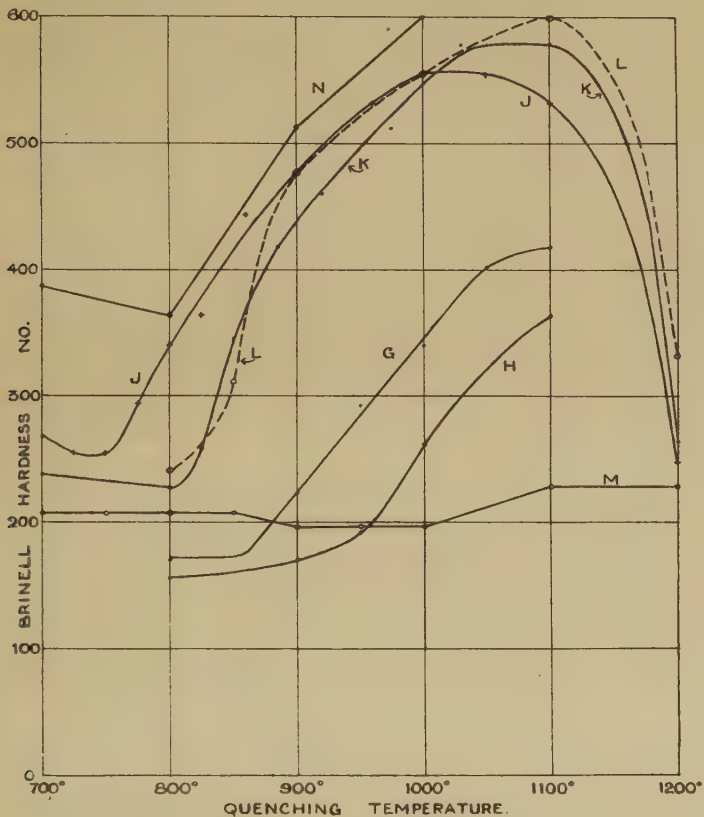


FIG. 51. Brinell hardness numbers obtained from various high chromium steels after quenching from the temperatures indicated :—

Curve.	Carbon %.	Chromium %.
G.	0.17	15.9
H.	0.17	17.1
J.	0.48	15.1
K.	0.53	16.8
L.	0.87	17.6
M.	0.42	25.0
N.	1.9	27.5

With a still higher chromium content, e.g., 25 to 30 per cent., material containing 0.4 per cent. carbon or thereabouts

is practically unaltered in hardness on quenching at any temperature up to 1,200° C.—see curve M. If the carbon content is increased to a considerably higher figure than this, however, such high chromium material hardens quite well—see curve N.

As a consequence of the lessened hardening power of stainless irons containing more than about 14 per cent. chromium, the tensile strength obtained after hardening and tempering such material is not so high as with the lower chromium irons; also, probably for the same reason, the high chromium irons have a rather lower ratio of yield point to maximum stress than those with less chromium. Typical properties, however, are indicated in the tests given in Table IX, and these show that very tough ductile material is obtainable. Probably such material as this will find its greatest use in the soft condition, either fully tempered or annealed, because, owing to its composition, it is extremely resistant to corrosion after any form of heat treatment.

TABLE IX

Mechanical Properties of High Chromium Stainless Iron.

Carbon %	Silicon %	Manganese %	Chromium %	Treatment.	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elongation % on 2 ins	Reduction of Area %	Izod Impact, ft. lbs.
0.09	0.21	0.13	14.4	O.H. 950° W.Q. 700° C.	35.6	40.0	29.0	66.8	107 107 117
0.10	0.10	0.23	14.4	A.H. 950° W.Q. 600° C.	22.0	34.4	34.0	65.8	70 67 70
0.10	0.23	0.14	14.4	A.H. 950° W.Q. 600° C.	28.8	37.4	31.0	63.7	80 70 80
				O.H. 950° W.Q. 700° C.	29.6	37.2	33.0	69.8	100 97 97
0.10	0.16	0.26	14.5	A.H. 950° W.Q. 600° C.	26.0	36.4	31.0	65.8	70 75 70
				O.H. 950° W.Q. 700° C.	23.6	35.2	34.0	69.8	108 107 108
0.09	0.26	0.15	15.2	O.H. 1050° W.Q. 600° C.	30.2	38.5	29.0	63.7	73 73 65
				O.H. 1050° W.Q. 700° C.	27.0	35.4	31.5	67.8	98 94 97
0.09	0.24	0.13	15.5	O.H. 1000° W.Q. 600° C.	40.0	46.9	22.0	61.5	62 75 55
				O.H. 1000° W.Q. 700° C.	31.3	40.0	28.5	61.5	78 80 88
				A.H. 950° W.Q. 600° C.	18.0	31.8	36.5	65.8	85 62 86
0.17	0.26	0.18	15.9	A.H. 950° W.Q. 700° C.	26.0	36.8	34.0	62.6	65 65 73
				A.H. 1000° W.Q. 700° C.	32.0	44.2	23.0	53.4	60 55 50
				O.H. 1000° W.Q. 700° C.	34.0	45.4	24.0	60.4	78 75 72

Irons with still higher chromium content and also higher carbon steels containing 20 or 25 per cent. of chromium, which

do not harden to any great extent, appear to give rather low impact figures although their tensile values are good ; thus a bar, one and one-eighth inches diameter, of material containing 0.10 per cent. carbon and 20.4 per cent. chromium, when oil quenched from 1,050° C., and tempered at 700° C., gave the following figures :—

Yield Point, tons per square inch.	Maximum Stress, tons per square inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Izod Impact, ft. lbs.
18.4	27.9	34.0	49.7	3. 2. 3.

while steel containing 0.42 per cent. carbon and 25.0 per cent. chromium, in the form of bars one inch in diameter, gave the results indicated below :—

	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Izod Impact, ft. lbs.
As Rolled ...	37.8	47.2	21.5	39.2	3 2 3
W.Q. 1,000° C. ...	26.0	42.8	26.5	51.0	1 2 1

It did not appear to be possible to improve these impact figures by any form of treatment.

Temper Brittleness. It is well known to makers and users of nickel chromium steels, and to a less extent of nickel steels, that there are certain limitations which have to be observed in the tempering of such steels if the maximum toughness, consistent with the required tensile strength, is to be obtained from them. Thus it is found that if samples of a nickel chromium steel are hardened and then tempered at successively higher temperatures, the toughness value does not increase uniformly with the tempering temperature. A sample tempered at 200° C. will be noticeably tougher than the untempered steel, but one tempered at 300° C. will be distinctly less tough than that tempered at 200° C. and probably less tough even than the untempered steel. Further, with increasing tempering temperature above 300° C., the toughness value only rises slowly until about 550° C., after

which it rises sharply. Moreover, the toughness of samples tempered at higher temperatures, e.g., 600° or 650° C., depends to a large extent on the rate at which they are cooled after tempering. If quenched from the tempering heat they give a fine grey fracture and a high impact value; on the other hand, if slowly cooled, they give a crystalline fracture and a low impact value, although the tensile strength may be the same in both cases. The difference in impact value is often very large, thus the figure from the rapidly cooled sample may be ten or twenty times the value from the slowly cooled piece.

These characteristics are found in some degree in other alloy steels (though generally to a less marked extent than in nickel chromium steels) and they may also be produced in carbon steels. It is important, therefore, to see to what extent they are found in stainless steels. As in these steels, the actual tempering temperatures used to obtain given effects differ from those in ordinary nickel and nickel chromium steels, the question may be explored under two heads:—

(a) In the range up to 500° C., in which the tensile strength does not materially alter, does the impact value increase regularly or is there any intermediate maximum value?

(b) Does the rate of cooling of samples tempered at 600° C., or above, alter the impact value obtained?

With regard to (a) it may be said definitely that the impact value does not generally increase uniformly with tempering temperature. Most samples give a maximum impact value when tempered between 200° and 400° C., so that increasing the temperature up to 500° C. tends to lower this value. There is, however, not the same regular variation in the impact value among different casts of stainless steel as there is, for example, with nickel chromium steels tempered at 200° and 300° C. Practically every piece of nickel chrome steel will show a drop in impact value after tempering at 300° C. In the case of stainless steel, some casts show a distinct drop in impact value when the tempering temperature is raised from 400° C. to 500° C., while with others, the toughness remains constant or even increases. Speaking generally, however, tempering in the range 200° to 400° C. is more likely to give maximum toughness for hardened material

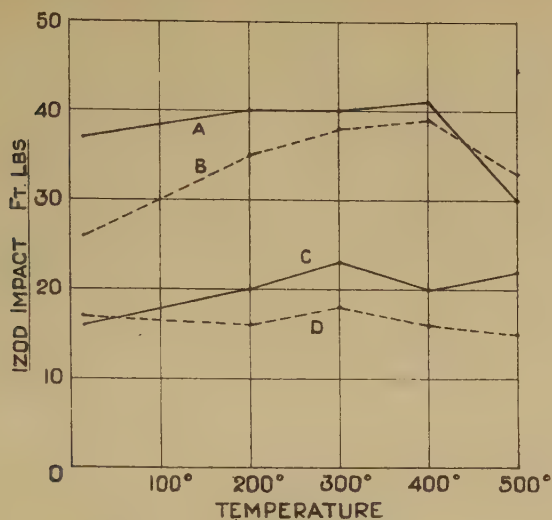


FIG. 52. Impact values obtained from hardened stainless steels after tempering up to 500°C.,:—

Curve.	Carbon, %	Chromium, %	How Hardened.	Average Brinell Hardness
				No.
A.	0.09	11.3	O.H. 950°	375
B.	0.16	13.0	O.H. 953°	430
C.	0.17	14.4	O.H. 950°	410
D.	0.23	12.8	A.H. 950°	437

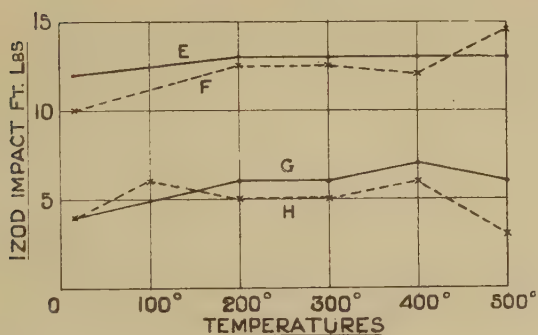


FIG. 53. Impact values obtained from hardened stainless steels after tempering up to 500°C.,:—

Curve.	Carbon, %	Chromium, %	How Hardened.	Average Brinell Hardness
				No.
E.	0.28	11.7	A.H. 900°	444
F.	0.29	11.7	A.H. 950°	444
G.	0.32	11.2	A.H. 900°	444
H.	0.50	12.2	A.H. 900°	477

than tempering at 500° C., and, as a general working temperature, 300° C. would probably be suitable. Figs. 52 and 53 show the results obtained from a variety of stainless steels and indicate the type of results obtained on tempering in this range.

The other phase of temper brittleness, as set out in paragraph (b), page 96, is also found in stainless steel, though to a less degree than in nickel chromium steels. Thus the following results were obtained on four casts of stainless steel containing 0.30 to 0.31 per cent. carbon. The samples were air hardened from 900° C., and then tempered at 700° C. The quickly cooled samples were quenched in water while the others were slowly cooled in a furnace, the time taken to cool to 400° C. being 10 to 12 hours.

Cast.	How Cooled.	Brinell Hardness No.	Izod Impact, ft. lbs.		
R. 1,051	{ Quickly	251	45	45	
	{ Slowly	251	22	21	20
R. 1,057	{ Quickly	241	44	38	38
	{ Slowly	235	25	23	25
R. 1,069	{ Quickly	255	35	38	30
	{ Slowly	248	19	19	19
R. 1,081	{ Quickly	258	47	44	38
	{ Slowly	255	37	33	30

A noticeable feature of the temper brittleness found in nickel chromium steels is that the susceptibility of different casts to the effect of rate of cooling after tempering varies considerably. Some casts very easily become brittle while other casts of the same chemical composition can be cooled at comparatively slow rates and still retain their toughness. A similar remark applies to stainless material; some casts of the steel are more susceptible than others. Thus each of the two casts of steel on which tests are given on page 99 when quenched in water after tempering, gave very high impact values as shown. With the slower rate of cooling obtained by allowing the bars (which were $1\frac{1}{8}$ inches diameter) to cool freely in the air from the tempering temperature, the impact value of one was lowered appreciably while the other was quite unaffected.

Cast.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0.25	0.21	0.22	12.2	0.20
B.	0.25	0.18	0.22	12.5	0.21

		Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact., ft. lbs.
A.	A.H. 925° W.Q. 700° C.	43.6	53.5	22.5	60.4	248	82 73 75
	„ A.C. 700° C.	—	—	—	—	241	45 45 51
B.	A.H. 925° W.Q. 700° C.	45.6	52.6	27.0	60.4	241	64 66 63
	„ A.C. 700° C.	—	—	—	—	255	64 62 68

It will thus be seen that the temper brittleness found in stainless steels has the same peculiarities as that found in nickel chromium steels and, as with the latter steels, although the precautions necessary to avoid its ill effects are known and can be applied to the various products, the actual cause of the brittleness is still unknown.

Effect of Size of Bar on Impact Tests. It was stated on page 80 that the results of mechanical tests obtained on bars of stainless material of about one inch diameter could be applied with certain restrictions to bars five or six times that size. With regard to the tensile tests, the results on the larger bars will be very similar to those on the one inch bars except that, under similar conditions of treatment, slightly lower values of the tensile strength may be obtained from the larger bars. The impact values obtained, however, tend to fall off when the size of bar exceeds two or three inches diameter. As an illustration, the following results obtained on steel of the following analysis:—

Carbon	0.30 %
Silicon	0.17 %
Manganese	0.23 %
Chromium	12.4 %
Nickel	0.55 %

may be quoted. Test A was obtained from a bar $1\frac{1}{8}$ inches diameter, while test B was taken from another, 4 inches

diameter, made from the same ingot which was twelve inches square. The heat treatment (O.H. 900° C., W.Q. 700° C.) was the same in each case.

		Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
A (1½" diameter)	...	39.4	51.6	24.0	59.8	241	73 65
B. (4" diameter)	...	39.0	51.0	25.5	57.0	241	37 34 31

The effect is due not so much to the difference in size of the pieces during the heat-treatment operation but probably to the fact that the larger bar has had less mechanical work during its manufacture.

From an examination of the results of the mechanical tests which have been given it will be evident that the properties of stainless steels compare very favourably with those of the very highest qualities of structural alloy steels. It will also be evident that the range of hardness and tensile strength available is ample for most engineering purposes.

Tests on Annealed Material. It has been pointed out earlier that the slow cooling of stainless steels, from temperatures above the carbon change point, produces structural results comparable with those obtained by the normalising, or slower cooling, of carbon steels. The mechanical properties of such annealed stainless material are also similar to those of normalised carbon steel and are characterised, when compared with the tests obtained from the same material when hardened and tempered, by low values of tensile strength and yield point, the fall in the latter being especially marked. The toughness and ductility values of annealed stainless steels depend to a very great extent on the temperature used for annealing.

The influence of annealing temperature on the micro-structure of the annealed sample was pointed out on page 36. The two types of structure referred to as "pearlitic" and "globular," obtained by annealing respectively at temperatures high enough to dissolve the whole of the carbide and in the range of temperature above Ac.1 in which the carbide is not wholly dissolved, are so widely different that it would be expected the mechanical properties given by

any one steel would vary with the type of structure obtained. The results obtained on a series of steels of differing carbon content after annealing at 880° and at 1,050° C., respectively are given in Table X.

TABLE X.

Mechanical Properties of Annealed Stainless Steel.

Composition.		Treatment.	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elonga- tion % on 2 ins	Reduc- tion of Area %	Brinell Hard- ness No.	Izod Impact, ft. lbs.
Car- bon. %	Chro- mium. %							
0.10	11.9 {	Annealed 880° C.	16.6	29.8	37.0	67.8	137	71 96 73
		Annealed 1,050° C.	22.0	30.3	40.0	73.6	137	39 41 20
0.14	11.6 {	Annealed 880° C.	17.2	35.8	34.0	65.8	163	27 27 27
		Annealed 1,050° C.	22.4	37.1	27.5	55.8	170	15 15
0.25	12.5 {	Annealed 880° C.	19.0	38.6	32.0	69.8	179	40 26
		Annealed 1,050° C.	22.0	41.3	26.0	47.2	192	8 5 8
0.32	12.7 {	Annealed 880° C.	18.4	41.1	29.0	65.8	179	23 15
		Annealed 1,050° C.	22.0	45.6	24.0	44.6	202	3 3

These results show the gradual increase in tensile strength and hardness accompanying an increase in carbon content. They also bring out very clearly the difference in the mechanical properties associated with the globular and pearlitic types of structure. This difference is least with the lowest carbon content, though one may note the big drop in the toughness value of this steel brought about by annealing at a high temperature. With the higher carbon steels, the differences are more marked and one may especially note the higher tensile strengths of the pearlitic samples and their very low toughness values. One may also observe that the samples annealed at 880° C. are not particularly tough when compared with the results obtained by hardening and tempering, especially if the low tensile strength of the annealed samples is taken into account.

Modulus of Elasticity in Tension (Young's Modulus). The results given in Table XI and obtained from a series of stainless steels with differing carbon content, show that the value of Young's Modulus of stainless steel is similar to that of carbon steel, though possibly somewhat

higher than the latter. The bars in all cases were oil hardened, sample A from 1,000° C., the others from 950° C., and then fully tempered at 700° to 725° C.

TABLE XI.

Modulus of Elasticity in Tension of Stainless Steel.

	A.	B.	C.	D.	E.
Carbon % ...	0.09	0.12	0.17	0.21	0.23
Chromium % ...	12.0	12.1	14.4	11.5	12.8
Max. Stress (tons per sq. inch) ...	43.5	41.3	44.6	53.4	50.2
Modulus of Elasticity (lbs. per sq. inch) ...	29.6×10^6	30.8×10^6	29.8×10^6	30.2×10^6	30.6×10^6

Determinations have also been made at Woolwich Arsenal on a series of steels* which had been oil hardened and tempered at various temperatures. In most cases the steels were hardened both from 950° and 1,000° C. and temperatures of 600°, 650° and 700° C. used for tempering. The range of tensile strength obtained from each steel and also the mean value of the modulus, is given in Table XII.

TABLE XII.

*Modulus of Elasticity in Tension of Stainless Steels
(Second Series).*

Steel.	Carbon. %	Silicon. %	Chromium. %	Range of Tensile Strength, Tons per sq. inch.	Mean Value of Young's Modulus, Lbs. per sq. inch.
1.	0.10	0.08	12.85	41.3 to 52.5	31.7×10^6
2.	0.15	0.11	13.5	43.6 to 59.8	31.2×10^6
3.	0.17	1.35	13.9	42.4 to 57.6	29.6×10^6
4.	0.31	0.31	14.2	48.7 to 67.7	32.1×10^6
5.	0.35	1.43	14.7	53.7 to 69.7	32.0×10^6
6.	0.43	0.13	12.37	50.4 to 63.9	32.3×10^6

These values are in good agreement with those given in Table XI.

* "Metallurgical Data on Stainless Steels." H. H. Abram. *Chem. & Met. Eng.*, Vol. XXX, p. 430 (1924).

Modulus of Elasticity in Shear. The figures obtainable from stainless steel are indicated by the results of the following torsion test obtained from material containing :—

Carbon	0.25 %
Silicon	0.18 %
Manganese	0.22 %
Chromium	12.5 %
Nickel	0.21 %

The test bar was air hardened from 925° C. and tempered at 675° C. and gave a Brinell hardness number of 255, corresponding to a tensile strength of 55 tons per square inch.

Stress at Limit of Proportionality	...	16.0 tons per square inch.
Stress at Yield Point	...	32.9 " " "
Maximum Stress	...	47.3 " " "
Total Twist in 4" (Test piece 0.5" dia.)	...	1140 degrees.
Modulus of Elasticity in Shear	...	12.5 × 10 ⁶ lbs. per sq. inch.

Fatigue Range of Stainless Materials. The problem of the strength of materials under alternating or repeated stresses is of the utmost importance in certain branches of engineering work. It has been known for many years that a stress which, if applied once or a few times to a metal part, would cause no apparent damage, might cause failure if repeated a very large number of times. Similarly, failure might occur if the stress alternated rapidly between positive and negative values (i.e., alternate tension and compression) over a considerable period of time. The failure of metals under such repeated or alternating stresses has been known under the general name of "fatigue" and many investigations have been carried out to determine the maximum ranges of stress which could be applied indefinitely to specific metals without causing failure. Until the last few years it was generally considered that the elastic limits in tension and compression represented the maximum stresses to which material could be submitted without fatigue, and hence the value of the elastic limit in tension (that in compression being similar in normal metals) was looked upon as the criterion of fatigue resisting properties. Recent work carried out by the Air Board in this country*, by Professors Moore and Kommers, of Illinois† and by others, have shown

* "Report on the Materials of Construction used in Aircraft and Aircraft Engines." H.M. Stationery Office. See also the recently published book, "Fatigue in Metals," by H. J. Gough.

† "An Investigation of the Fatigue of Metals." H. Moore and J. B. Kommers Eng. Expl. Station; Univ. of Illinois. *Bulletins* Nos. 124, 136, 142.

that there is no apparent connection between the elastic limit in tension (or the yield point for that matter) of a material and its fatigue range. On the contrary, the only figure in the tensile test which showed any regular relation to the fatigue range was the maximum stress and this relation was only approximate.

These investigations showed that in the case where the stress alternated between positive and negative (i.e., tension and compression) values of the same magnitude, the total safe range of stress (i.e., the sum of the tension and compression values), or the "fatigue range" as it is called, was 90 to 100 per cent. of the maximum stress in tension; in other words, the fatigue range of a material having a tensile stress of 100 tons per square inch, would be between ± 45 and ± 50 tons, the maximum tension and compression values of the range each being 45 to 50 per cent. of the maximum stress. While this relationship held for quite a number of metals, those tested being mainly ferrous metals, it was not universal, certain exceptions being found. As an indication of the type of agreement found among ferrous metals, however, the results given in Table XIII are taken from the Air Board publication mentioned earlier:—

TABLE XIII.

Fatigue Ranges of Various Steels.

Material.	Elastic Limit, Tons per sq. inch.	Maximum Stress, Tons per sq. inch.	Fatigue Range, Tons per sq. inch.	Ratio of Fatigue Range to	
				Elastic Limit.	Max. Stress.
Case Hardening Steel	17.6	39.5	± 18.4	2.09	.94
3 % Nickel Case Hardening Steel ...	16.0	65.5	± 31.0	3.88	.94
5 % " " " " " " ...	14.0	60.0	± 30.0	4.30	1.0
6 % " " " " " " ...	20.0	57.8	± 26.5	2.65	1.02
Air Hardening Nickel Chrome Steel,					
Hardened	20.0	109.1	± 45.5	4.55	.84
" " " Temp. 200°	36.2	101.2	± 51.5	2.85	1.02
" " " " 400°	53.3	97.9	± 47.5	1.78	.98
" " " " 500°	51.7	82.4	± 41.5	1.61	1.00
" " " " 600°	40.9	70.1	± 35.5	1.74	1.00
Nickel Chrome Steel, Oil hardened					
and tempered	55.0	65.7	± 33.0	1.20	1.00
Chrome Vanadium Steel, Hardened					
and tempered	44.8	62.9	± 32.8	1.46	1.04
Mild Steel, Normalised	23.1	37.9	± 17.0	1.47	.90
" " Hardened and tempered	25.4	46.8	± 19.0	1.50	.82
Mild Steel, Cold worked	18.2	40.8	± 19.1	2.1	.91
" " " Tempd. 250° C.	20.5	40.1	± 18.4	1.8	.92
" " " " 400° C.	28.1	39.9	± 19.0	1.35	.95
" " " " 550° C.	25.0	36.8	± 18.0	1.45	.98

It will be seen from these tests that the ratio between fatigue range and maximum stress is fairly constant ; on the other hand there is no apparent relation between fatigue range and elastic limit.

So far as the author is aware no very extensive investigation has been carried out on the fatigue range of stainless material ; the following results, however, indicate that this material falls in line with the steels which were tested by the Air Board.

The material used for these tests contained 0·12 per cent. carbon and 12·1 per cent. chromium. The bars were hardened and tempered giving the following mechanical properties.

Elastic Limit...	...	16·1 tons per square inch.
Yield Point	30·3 " " "
Maximum Stress	43·1 " " "
Elongation	...	33·5 %
Reduction of Area	...	66·8 %
Izod Impact	94, 85, 88 ft. lbs.

Values of the fatigue range were obtained :

- (1) By testing a number of samples at gradually increasing stresses, and determining the stress at which the material withstood 4,000,000 reversals of stress without breaking.
- (2) Using the method developed by H. J. Gough, at the National Physical Laboratory, in which the deflection of the revolving test piece under gradually increasing load is plotted against the load, the point where the deflection no longer ceases to be proportional to the load being taken as the fatigue limit.

The values obtained by these methods were :—

- (1) \pm 21·5 tons per square inch.
- (2) \pm 23·1 tons per square inch.

These figures give values of 1·0 and 1·07 for the ratio of fatigue range to maximum stress.

Investigations carried out by D. J. McAdam* on a stainless steel containing 0·21 per cent. carbon, 0·79 per cent. silicon, 0·59 per cent. manganese and 13·31 per cent.

* *Chem. & Met. Eng.*, Vol. 25, p. 1081.

chromium, gave similar results. Suitably hardened and tempered samples of this material, having a tensile strength of 43.5 tons per square inch, had a fatigue range, for a hundred million cycles of stress, of 21.0 tons per square inch, corresponding to a value of 0.965 for the ratio of fatigue range to maximum stress.

It would appear, therefore, from the somewhat meagre data available, that the value of the limiting stress which may be applied alternately in tension and compression to stainless material is approximately half the maximum stress in tension and that stainless steel, therefore, behaves in a similar manner as regards fatigue to other ferrous materials.

Mechanical Tests at Temperatures above Atmospheric. The use of stainless steel for a variety of purposes in which it is liable to be stressed while heated to varying temperatures above that of the atmosphere, makes it important that the properties of the material at such temperatures should be determined. The following figures, it is hoped, will enable the engineer to form some idea of the relative strength of stainless steels and other steels at such temperatures.

The determination of the tensile strength of steel at temperatures up to about 500° C. does not present any great difficulties. The test piece, turned to suitable dimensions, is placed in the jaws of a testing machine and is heated there, by a suitably designed furnace, to the required temperature. After holding at that temperature for a sufficiently long time to ensure uniformity, it is pulled while still hot and without removing the furnace, the actual testing operation differing little from that on pieces tested under ordinary conditions. Above about 500° C., however, all steel is more or less plastic and hence the results obtained are dependent to a greater or less extent, according to the actual temperature, on the speed of pulling. That this is the case has been known for some considerable time. It was hardly realised, however, to what an extent steel behaved like a viscous fluid at comparatively low temperatures until J. H. S. Dickenson published the account of his remarkable investigations on the flow of steels at a low red heat.* Dickenson showed that, at temperatures of 500° C. and upwards, both ordinary

* "Some experiments on the flow of steels at a low red heat, with a note on the scaling of heated steels." J. H. S. Dickenson. *J.I.S.I.*, 1922, II, p. 103.

steels and alloy steels of various types would stretch plastically and finally break under loads which were very considerably less than the figures for maximum stress obtained from carefully conducted tensile tests at the same temperatures. Thus a sample of mild steel containing 0.3 per cent. carbon which had a maximum stress of 20.8 tons per square inch, when tested in the ordinary way at 600° C., actually broke after being loaded continuously, for 956 hours at a temperature of 550° to 600° C., with a load equal to 8.5 tons per square inch. In the same way a sample of high speed steel broke under the same load (8.5 tons per square inch) after 564 hours in the range 650° to 700° C., although a tensile test at 700° C. had indicated a tensile strength for this material of 23 tons per square inch at this temperature. In addition, at temperatures lower than those given above, the materials stretched continuously under the same load and no doubt would have broken eventually. Perhaps the most remarkable result obtained was that of a nickel-chromium-iron alloy which was loaded equivalent to 8.5 tons per square inch while being kept in the range 600° to 650° C. It supported the load for 6,041 hours, though continuously stretching from the first day, and then broke at the end of this period although such material, when tested in the ordinary way at 700°, would give a maximum stress of 27 to 30 tons per square inch. It is perfectly evident from a consideration of Dickenson's figures, that all ferrous materials behave like viscous fluids at temperatures above about 500° C., and hence that the figures obtained from tensile tests at higher temperatures than this do not represent the load the material will stand when continuously loaded for long periods. At the same time, however, such figures for tensile strength, if carefully obtained under strictly comparable conditions, certainly give some indication of the relative life of the different materials when stressed at such temperatures and have, therefore, a distinct value in this respect. The figures which are quoted later regarding tests on various materials at high temperatures should be interpreted in this light.

From an engineering point of view, the strength of materials in the range of temperature met with in the use of superheated steam is of considerable importance. Results already quoted have shown that hardened stainless material

resists tempering up to $500^{\circ}\text{C}.$; in addition it retains its strength and hardness very well when heated in this range of temperature.

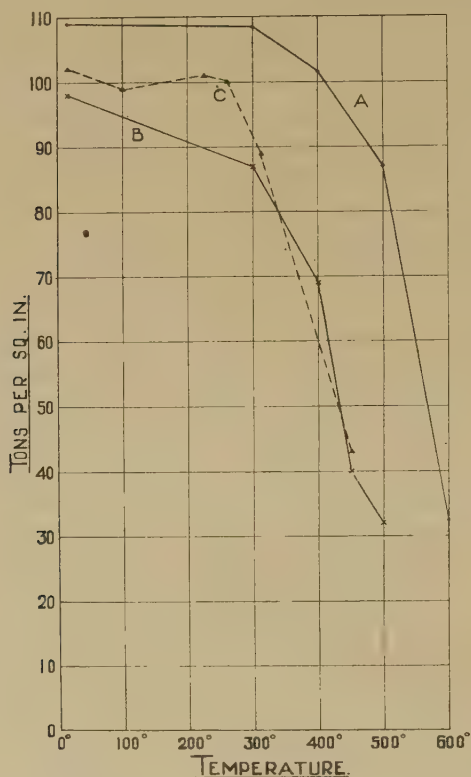


FIG. 54. Tensile strength of hardened steels at temperatures up to $600^{\circ}\text{C}.$:—

Curve A. Stainless Steel.

Curve B. Ordinary Steel, 1.0 per cent. carbon.

Curve C. " " 0.5 per cent. carbon.

In Fig. 54 are plotted the results obtained by Dr. W. H. Hatfield,* of tensile tests on stainless steel hardened and tempered to give about 110 tons per square inch when tested at temperatures up to $600^{\circ}\text{C}.$ For comparison, results obtained by Professor F. C. Lea, on two carbon steels containing, respectively, 1.0 and 0.5 per cent. carbon and treated to give approximately the same hardness as that of the

* "Stainless Steels." Dr. W. H. Hatfield. *Coventry Engineering Society Journal*, June, 1923, p. 126.

stainless steel, are included.* These show that whereas the tensile strength of the high carbon steel fell to 69 tons per square inch at 400° C., 40 tons at 450° C., and 32 tons at 500° C. (that containing 0·5 per cent. carbon giving similar values), the stainless steel retained almost its full strength at 400° C. and gave 87 tons per square inch at 500° C. It follows from these results that articles such as valves, which

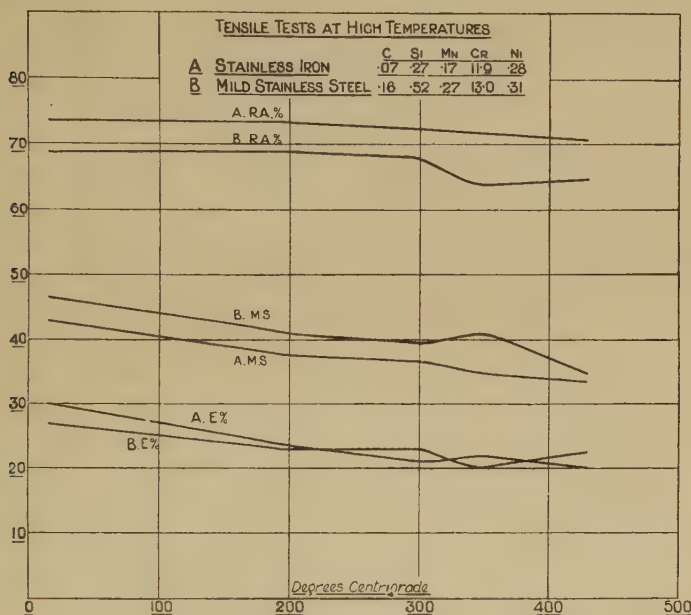


FIG. 55. Tensile tests of hardened and tempered samples of low carbon stainless steels at temperatures up to 500° C.

are exposed to temperatures such as are obtained with superheated steam, are, therefore, much more likely to wear better if made of hardened stainless steel than if made from ordinary steel, and this apart from any question of corrosion.

Stainless material which has been hardened and fully tempered also retains its strength well in the same range of temperature. Figs. 55 and 56 give the results of tests carried out on stainless material of differing carbon content while, in Fig. 57, values for the maximum stress of these materials

* "The Effect of Temperature on some of the Properties of Metals." Prof. F. C. Lea. *Proc. Inst. Mech. Eng.*, 1922, II, 885.

are plotted along with those of a number of other engineering metals for comparison. The results show that the tensile strength of stainless material in the range of temperature up to 500° C. possesses an evenness and regularity which is equalled by few other materials while many are distinctly inferior.

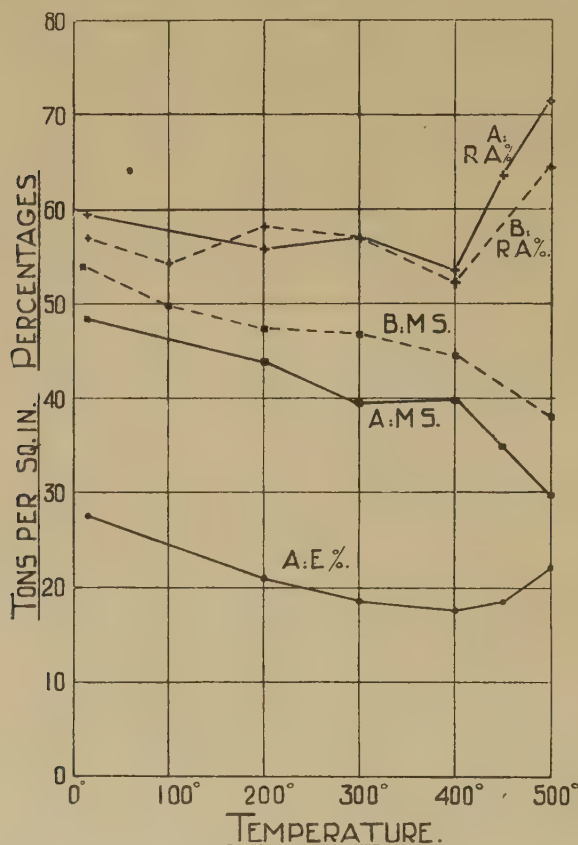


FIG. 56. Tensile tests of hardened and tempered samples of stainless steels at temperatures up to 500°C. :—

	Carbon, %	Chromium, %	Previous Treatment.
A.	0·36	11·2	A.H. 900. W.Q. 700° (<i>Author</i>).
B.	0·26	14·7	O.H. 925. T. 650° (<i>J. H. S. Dickenson</i>).

At temperature above about 500° C., Dickenson's work, referred to above, showed that the tensile tests ordinarily obtained by testing at these temperatures do not by any means indicate the maximum load the material will sustain

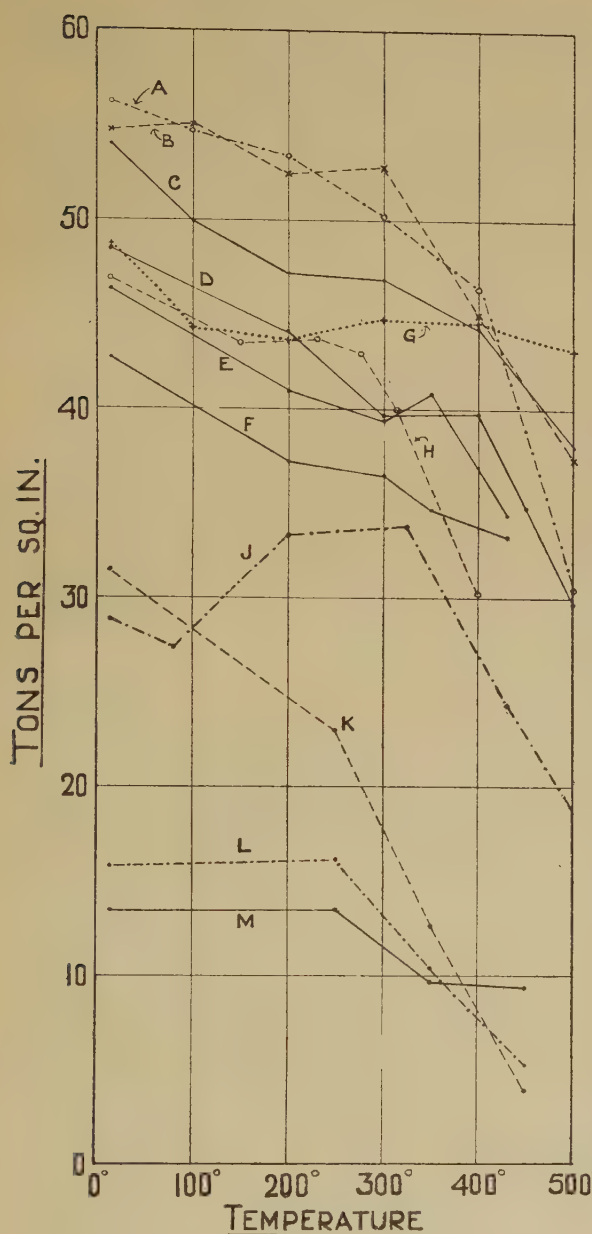


FIG. 57. Tensile strength of various engineering materials at temperatures up to 500°C. :—

- A. Nickel Chrome Steel (*Author*).
 B. High Speed Steel (*Dickenson*).
 C. Stainless Steel (*Dickenson*).
 D. " " (*Author*).
 E. " " "
 F. " " "
 G. Nickel Chromium Alloy (65% Nickel, 12% Chromium) (*Dickenson*).
 H. Monel Metal (*Aitchison*).
 J. Mild Steel (*Le Chatelier*).
 K. Muntz Metal (*Aitchison*).
 L. Gun Metal (*Aitchison*).
 M. Phosphor Bronze (*Aitchison*).

when loaded for long periods. If such tests are taken carefully under standardised conditions, however, they appear to give relative information regarding the behaviour of the materials under more prolonged loading. Thus, if one material A gives a tensile strength at, for example, 700°C ., which is about twice as much as that given under similar conditions by a second material B, one can reasonably expect that under service conditions involving either continuous or intermittent loading over long periods at that temperature, material A would deform much less slowly and, therefore, have a longer serviceable life than B. Interpreted

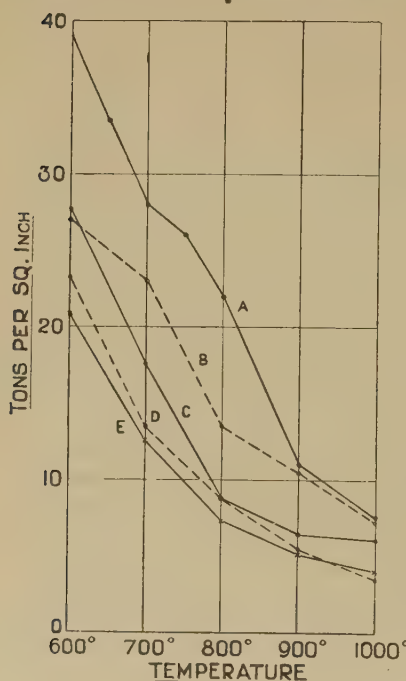


FIG. 58. Tensile strength of steels at high temperatures (*Dickenson*):—

- A. Nickel Chromium Alloy. 65 % nickel, 12 % chromium.
- B. High Speed Steel. 14 % tungsten.
- C. Stainless Steel. 0.26 % carbon, 14.68 % chromium.
- D. Nickel Chrome Steel. 0.25 % carbon, 3.63 % nickel, 0.55 % chromium.
- E. Mild Steel. 0.30 % carbon.

* loc. cit.

in this way, high temperature tensile tests would appear to the author to have a distinct value, although it is quite obvious that they do not give definite information as to the maximum load which a given material will stand at some specified temperature.

Such comparative tests carried out by *Dickenson** on a number of steels have given values which are plotted in Fig. 58. These indicate that, at such high temperatures, the strength (and also the hardness) of stainless steel is considerably greater than that of either ordinary mild steel or of the ordinary types of structural alloy steel, but is not so great as that of high speed steel or of the high nickel chromium alloys. By increasing the carbon content of stainless steel, the tensile strength at high temperatures is correspondingly increased.

The results of these tests agree with practical expe-

rience as regards the hot working of such steels and alloys. Stainless steel is distinctly harder to work at the temperatures given in Fig. 58 than ordinary steel or the type of structural alloy steel quoted. It is also harder to work, the higher its carbon content. On the other hand, it is more easily worked

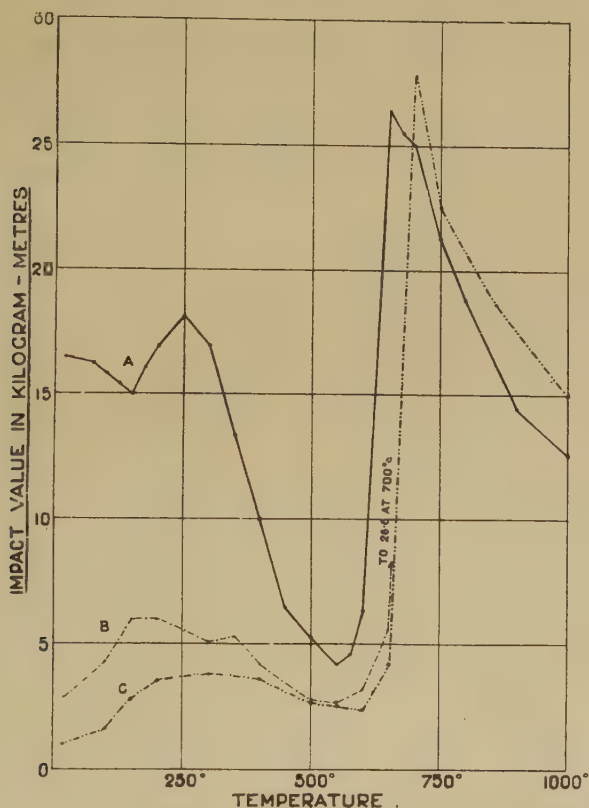


FIG. 59. Impact values of ordinary steels at high temperatures:—

- A. 0.23 % carbon.
- B. 0.47 % "
- C. 0.73 % "

than either high speed steel or the high nickel chromium alloys. Similar relative behaviour may also be noted when these various materials are used in practice under conditions which involve deformation at high temperatures, such as are met with, for example, in the case of exhaust valves of internal combustion engines.

In addition to the effect of high temperatures on the strength or hardness of engineering materials, it is important to know how such temperatures affect their toughness. Thus it is well known that ordinary carbon steel has a brittle range, known as "blue brittleness," at temperatures rather less than those showing a faint colour of heat, roughly between 300° and 500° C. The best means of measuring this brittleness is to use some form of the notched bar impact test. With such a test it is almost impossible to have a furnace round the test piece while it is being broken; however, if the test piece is heated to the required temperature, transferred rapidly to the testing machine and immediately broken, the loss of temperature occurring in the short interval between drawing the test piece from the furnace and breaking it, is very small so that the temperature of the test piece at the moment of breaking may be regarded as being the same as that of the furnace without appreciable error. In the experiments described below, the test pieces were 10 mm. square and were notched with the standard Vee notch, as specified in the Izod test; they were broken, however, in a Charpy machine instead of an Izod machine because the test piece may be more rapidly placed in position and broken in that machine.

Tests on ordinary carbon steels containing differing amounts of carbon show that the range of "blue brittleness" is well indicated by the notched bar test. This is shown by the values obtained from such steels which are plotted in Fig. 59. The curves in Fig. 60 show that a similar brittle range occurs in several of the structural alloy steels in common use. It will be noticed, in all these curves, that the impact value rises sharply to a maximum about 700° C. and then falls gradually. At temperatures below that at which the maximum impact value is obtained, the test pieces fracture under the test; at this temperature and above they no longer break but bend, and the gradually falling impact value in the range 700° to $1,000^{\circ}$ C. is due to the material becoming softer with increasing temperature and, therefore, requiring a smaller expenditure of energy to bend it. With stainless steel, the relationship between toughness and temperature is quite different. The curves in Fig. 61 show the results obtained on stainless steels of different carbon content; with these materials, the impact value is much more

uniform as the temperature rises ; there is no range of " blue brittleness " as with carbon steels or with the structural alloy steels described in Fig. 60.

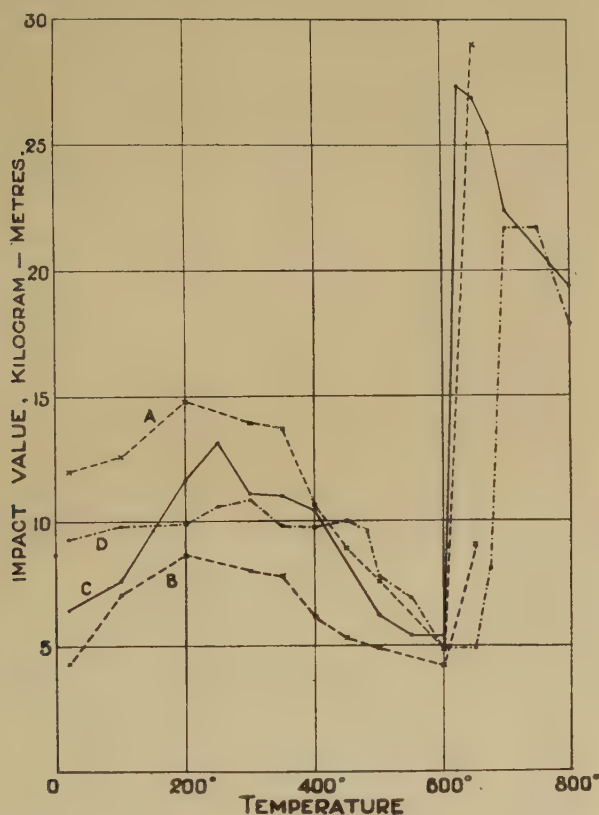


Fig. 60. Impact values of various structural alloy steels at high temperatures :—

Curve.	Steel.	Carbon, %	Nickel, %	Chromium, %	Previous Treatment.
A.	3 % Nickel.	0.32	3.34	0.02	O.H. 830° WQ. 650°C.
B.	3 % Nickel.	0.32	3.34	0.02	A.H. 830°C.
C.	5 % Nickel.	0.36	4.87	—	O.H. 830° WQ. 625°C.
D.	Nickel Chrome.	0.31	3.50	1.58	A.H. 830° WQ. 650°C.

The bearing of these results on the use of material for certain engineering purposes is obvious. Many cases occur in which parts of engines or machines are subjected to stress at temperatures of 300°, 400° or even 500° C. The absence of any brittle range in stainless material at these temperatures and the fact that the impact value

at high temperatures is sensibly the same as that at ordinary temperatures give the engineer a considerable measure of security that this material is not likely to break under shock in certain ranges of temperature and, at the same time, he will know that the results obtained from impact tests carried out at ordinary temperatures represent values of the same order as those which would be obtained if the testing were carried out at higher temperatures.

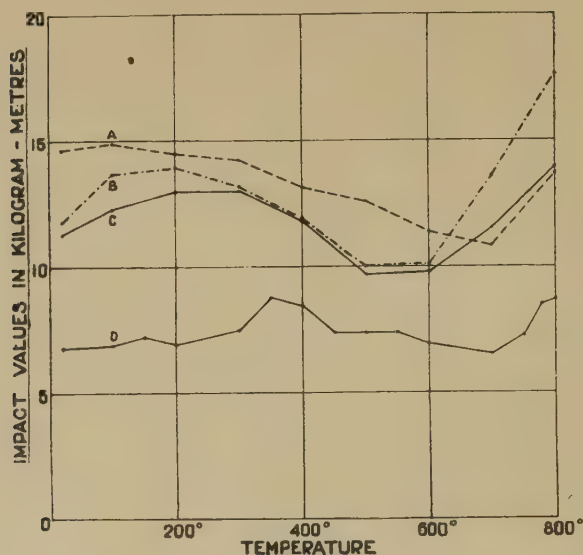


FIG. 61. Impact values of stainless steels at high temperatures :—

Curve.	Carbon, %	Chromium, %
A.	0.10	13.6
B.	0.15	13.0
C.	0.21	13.5
D.	0.34	11.2

The Influence of Various Alloying Metals on the Physical Properties of Stainless Steel. Apart from chromium and carbon, the most frequent variations in the composition of stainless steel are in respect of silicon and nickel. Manganese may also vary slightly but, in general, is fairly constant. Occasionally small quantities of aluminium are present whilst copper has been suggested as a suitable addition. In the following paragraphs the

effect of varying amounts of these elements is dealt with briefly.

(a) **Silicon.** A considerable amount of low carbon stainless material containing up to about 1 per cent. of silicon, in some cases even 2 per cent., has been put on the market. Its presence in such low carbon material is understandable owing to melting conditions involving the use of ferro-silicon as a reducing agent, although such low carbon material can be produced quite readily with a low silicon content. There is not the same reason for its presence in higher carbon material and generally, when found in this, it has been added purposely.

The effect of the presence of notable amounts of silicon is to raise the carbon change point of the steel quite considerably and also to diminish to some extent its air hardening capacity. The effect on the temperature at which Ac.1 occurs is indicated approximately by the following figures :

Per cent. Silicon	0.17,	1.85,	3.50
Temperature of Ac.1	805° C.,	885° C.,	975° C.

The position of the point, however, is affected by the chromium content and probably by the amount of carbon present as well.

In order to produce in high silicon steels the same hardening effect and also the same solution and diffusion of the carbide, an important matter from the point of view of corrosion, a considerably higher temperature is required for hardening than in steels low in silicon, a matter of some importance in the practical treatment of the steel.

The effect of silicon on the mechanical properties of the steel is noticeable in two directions. In the first place the silicon retards the tempering of the steel so that, when hardened and then tempered at 700° C. or thereabouts, the silicon steel is rather harder than a similar steel low in silicon ; secondly, under similar conditions of hardening and tempering, silicon is very liable to reduce the toughness of the material, often to a considerable extent. These effects are well illustrated by the following series of results obtained at the Research Department, Woolwich Arsenal.*

* "Metallurgical Data on Stainless Steels." H. H. Abram. *Chem. & Met. Eng.*, Vol. XXX, p. 430 (1924).

In this investigation, two grades of steels were used, with low carbon and high carbon respectively, and having the analyses given below :

Mark.	Carbon	Silicon	Chromium
A.	0.15	0.11	13.5
B.	0.17	1.35	13.9
C.	0.31	0.31	14.2
D.	0.35	1.43	14.7

Two series of tests were obtained. In the first series the bars were oil hardened at 950° C. and subsequently tempered at various temperatures. As, however, the high silicon steels were not effectively hardened from 950° C., a further series of test bars were oil hardened from 1,000° C. and then tempered at the same series of tempering temperatures as before.

The results obtained from these two series of tests are given in Tables XIV and XV.

TABLE XIV.

Influence of Silicon on the Mechanical Properties of Stainless Steel.

SERIES I. OIL HARDENED, 950° C.

Steel	Carbon. %	Silicon. %	Tempering Tempera- ture	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.		
A.	0.15	0.11	600° C.	50.5	59.8	21	63	285	27	29	26
			650° C.	39.5	49.4	24	66	233	37	38	41
			700° C.	32.4	43.6	28	69	206	109	103	109
B.	0.17	1.35	600° C.	30.2	46.2	27	62	229	9	10	8
			650° C.	30.0	44.5	27	64	222	14	13	13
			700° C.	27.5	42.2	32	67	210	15	14	14
C.	0.31	0.31	600° C.	54.0	65.4	18	55	305	31	33	24
			650° C.	43.0	55.6	23	60	262	39	35	37
			700° C.	35.0	48.7	28	67	228	64	63	63
D.	0.35	1.43	600° C.	49.0	62.7	19	54	296	13	13	14
			650° C.	44.5	58.8	22	55	274	16	18	16
			700° C.	38.5	53.7	27	59	249	24	23	23

TABLE XV.

*Influence of Silicon on the Mechanical Properties of
Stainless Steel.*

SERIES II. OIL HARDENED, 1,000° C.

Steel.	Carbon. %	Silicon. %	Tempering Temperature.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.
A.	0.15	0.11	600° C.	47.0	57.0	22	63	317
			650° C.	40.0	50.0	25	65	280
			700° C.	32.5	43.8	29	67	244
B.	0.17	1.35	600° C.	44.5	57.6	22	57	276
			650° C.	39.5	53.6	24	60	259
			700° C.	35.5	49.8	27	61	238
C.	0.31	0.31	600° C.	54.0	67.7	19	50	317
			650° C.	45.0	59.4	23	56	280
			700° C.	37.0	52.2	26	62	244
D.	0.35	1.43	600° C.	55.0	69.7	19	50	326
			650° C.	50.0	65.1	21	53	301
			700° C.	42.5	58.2	24	57	270

The first series of tests shows very clearly the embrittling effect of the silicon but does not show the hardening effect so well because the high silicon steels (especially that containing the lower carbon) were not fully hardened. Series II, however, shows the hardening effect very well.

Values for Young's Modulus of Elasticity were also obtained from these four steels and they indicate that silicon has no noticeable effect on the elasticity of the steel. The mean values for each steel after hardening and tempering are given in Table XVI.

TABLE XVI.

*Effect of Silicon on the Modulus of Elasticity of
Stainless Steel.*

Steel.	Carbon. %	Silicon. %	Chromium. %	SERIES I.	SERIES II.
				O.H. 950° C. and tempered. Lbs. per sq. inch.	O.H. 1,000° C. and tempered. Lbs. per sq. inch.
A.	0.15	0.11	13.5	31.5×10^6	30.9×10^6
B.	0.17	1.35	13.9	29.5×10^6	29.6×10^6
C.	0.31	0.31	14.2	32.2×10^6	32.0×10^6
D.	0.35	1.43	14.7	32.4×10^6	31.6×10^6

Although the presence of about one per cent. silicon has, undoubtedly, a very great tendency to reduce the toughness of the stainless material to which it is added, it may be noted that such reduction of toughness does not always occur if the carbon content is low, i.e., 0.10 per cent. or thereabouts. Some casts of material containing such an amount of silicon give very good impact values while other casts, of similar analysis, give low values. The cause of such variations is obscure as the steels may be made under apparently identical conditions. The variation may be illustrated by the following tests obtained from a series of casts made during the course of one week in a 7-ton electric furnace. The bars tested were one inch diameter, and were hardened in oil from 950° to 975° C. and subsequently tempered at 700° C.

Cast.	Carbon. %	Silicon. %	Chromium. %	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduction of Area per cent.	Izod Impact, ft. lbs.		
R 1005	0.11	0.89	12.5	30.4	44.0	25.0	52.2	77	67	67
R 1008	0.09	0.77	12.0	35.2	42.6	30.0	67.8	104	105	102
R 1010	0.09	1.06	12.4	30.0	40.0	30.0	59.3	78	97	77
R 1012	0.12	1.08	12.1	31.0	42.8	30.5	60.4	74	69	59
R 1014	0.14	1.08	12.2	30.0	43.6	33.0	64.8	28	25	27

The first four casts were relatively tough, although their actual toughness value varied; the fifth, made apparently under the same conditions, gave a very much lower impact value.

Microscopically, the effect of the presence of silicon in appreciable quantity in low carbon material is to retard the solution of the free ferrite while, even when a sufficiently high temperature is reached to dissolve this ferrite, it readily separates out again on cooling, such separation occurring even when the material is quenched in the form of small samples. The effect may be illustrated by Fig. 62, which shows the structure of material containing:—

Carbon	0.09	%
Silicon	1.06	%
Manganese	0.29	%
Chromium	12.4	%
Nickel	0.40	%



FIG. 62. Stainless iron containing 1.06 per cent silicon after oil quenching from 1,100°C. $\times 100$. Note presence of large amount of free ferrite.

To face page 121.]

after oil quenching from $1,100^{\circ}\text{C}$. in the form of a one inch bar. The amount of free ferrite was not lessened by soaking at this temperature (previous to quenching) for four hours. Material low in silicon but otherwise similar in analysis would be quite free from ferrite after such treatment. The free ferrite in such high silicon stainless iron is also very liable to form very large grains, producing quite an extraordinary degree of brittleness.

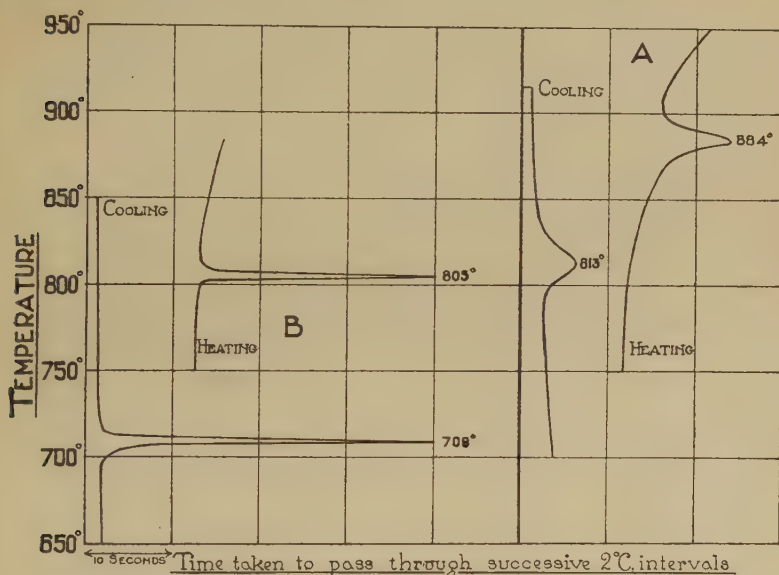


FIG. 63. Effect of high silicon content on the heating and cooling curves (inverse rate) of high carbon stainless steel (see page 122):—

No.	Carbon, %	Silicon, %	Chromium, %
A.	0.96	1.86	13.7
B.	0.96	0.17	13.1

(Note the spreading out and relative indefiniteness of the change points in steel A as compared with the sharply defined arrests on the curves from steel B.)

From several points of view the properties induced in low carbon stainless steel by the presence of about one per cent. of silicon would be useful. Thus, although stainless iron does not air harden to anything like the same extent as the higher carbon steel, it certainly does harden in some degree, and the reduction of this limited capacity for air hardening by the presence of the silicon would be valuable for certain purposes. Again the effect of the silicon in raising the

temperature at which the Ac.1 range commences is useful commercially as it increases the tempering range of the steel, an effect obviously of value where the production of soft material is essential. Unfortunately, however, these good qualities are off-set by the liability to produce brittleness so that in cases where tough ductile material is essential, the presence of silicon is very dangerous.

The presence of silicon in stainless steel also appears to have the peculiar effect of making the Ac.1 point very indistinct on thermal curves, even when the steel contains a large amount of carbon. This may be noticed in the inverse rate curves* given in Fig. 63, and relating to steel containing about one per cent. carbon. Although this matter is probably more of theoretical interest, it has a practical importance in that the determination of the Ac.1 point in high silicon steels by ordinary thermal curves is more difficult than in low silicon steels.

With still higher percentages of silicon, the effect on the impact value obtainable from the material becomes very marked and in addition very high temperatures are required to produce any hardening effect in the steel, particularly if the chromium content is also high. The following values were obtained from half-inch square bars of material of the analysis given and they illustrate the characteristics described above.

Composition.			Treatment.	Brinell Hardness No.		Izod Impact, ft. lbs.	
Carbon %	Silicon %	Chromium %		After Hardening.	After Tempering.		
0.15	3.5	8.7	W.H. 950° W.Q. 700°	228	228	4	4
			W.H. 1,050° W.Q. 700°	364	282	4	4
			A.H. 1,050° W.Q. 650°	241	235	3	4
0.22	3.3	14.9	W.H. 950° W.Q. 700°	228	228	2	3
			W.H. 1,050° W.Q. 700°	235	228	2	2

All the impact fractures were coarsely crystalline

(b) **Nickel.** Most samples of stainless steel contain small amounts of nickel, generally less than one per cent.

* In these curves the ordinates are respectively temperature and the time taken to pass through successive small temperature intervals, each 2° C.

As a rule, this nickel is not purposely added, but comes from the materials used in making the steel.

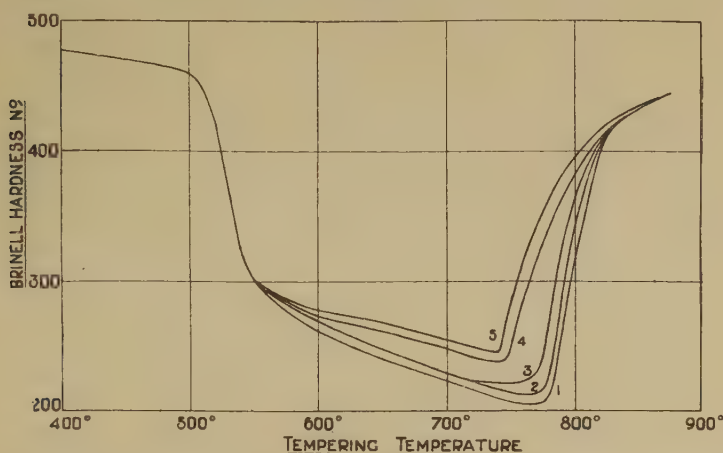


FIG. 64. Effect of Nickel on the hardening and tempering of stainless steel:—

No.	Carbon, %	Chromium, %	Nickel, %
1.	0.34	11.3	0.26
2.	0.38	11.0	0.60
3.	0.33	11.0	0.98
4.	0.41	11.2	1.25
5.	0.38	11.1	1.60

The action of nickel, in many respects, is the reverse of that of silicon. Instead of raising the temperature of the critical changes, nickel, when present in appreciable amounts, lowers them quite considerably. At the same time it increases materially the air hardening capacity of the steel. Like silicon, however, it retards the tempering of the steel. The influence of nickel on the hardening and tempering of stainless steel may be illustrated by the curves on Fig. 64. These represent the Brinell hardness numbers obtained from a series of five stainless steels in which the nickel content varied from 0.26 to 1.60, the composition with regard to other elements being sensibly constant. The samples were first oil hardened from 900° C. and were then tempered at gradually increasing temperatures. They were quenched out in water from each tempering heat and were Brinelled at each stage. The results indicate that nickel has no appreciable effect on the hardness of the steel after hardening at 900° C. or when subsequently tempered up to 550° C.

Above that tempering temperature, however, the nickel retards the tempering considerably, causing the high nickel steels to be distinctly harder after tempering at a given temperature than those with lower nickel content. In addition, owing to the effect of nickel in lowering the temperature at which the A_{c1} change occurs, the tempering range of the high nickel steels is considerably shortened; this, by precluding the use of the highest tempering temperatures available with a steel of low nickel content, also increases the difference between the maximum softness obtainable on tempering steels of low and high nickel content. The effect is probably exhibited in the most striking manner by comparing the results obtained from steels, Nos. 2 and 5 in Fig. 64. These two steels, except for their nickel content, are almost identical in analysis. The former with 0.6 per cent. nickel, after tempering at 750° to 775° C., gave a Brinell hardness number of 215, equivalent to a tensile strength of 46 to 47 tons per square inch. On the other hand, steel No. 5, with 1.6 per cent. nickel, reached its maximum softness at 720° C. to 740° C., giving a Brinell hardness number of 244, equivalent to a tensile strength of 53 tons per square inch. Tempering the two steels at 700° C. gave hardness numbers of 228 and 255, respectively, these being equivalent to tensile strengths of 50 and 55 tons per square inch.

The influence of nickel in intensifying the air hardening capacity of the steel may perhaps be illustrated by figures obtained from experiments carried out with the object of finding the necessary conditions for annealing the high nickel steels, in other words, determining the fastest rate of cooling which will prevent the steel from hardening. Samples of steels Nos. 1 and 5 (Fig. 64) were heated to 900° C. and, after soaking for half-an-hour, were transferred to furnaces at 700° , 650° or 600° C. (being air cooled approximately to the temperature of the second furnace before placing therein) and soaked at these temperatures for varying periods after which they were quenched out in water and subsequently Brinelled. The method of treatment is, of course, that recommended for annealing the steel and described on page 61. A similar series was also carried out using an initial temperature of $1,060^{\circ}$ C. The results obtained are given in Table XVII.

TABLE XVII.

Initial Temperature.	Steel No.	Nickel %	Time in Second Furnace	Temperature of Second Furnace.		
				700° C.	650° C.	600° C.
900° C.	1	0.26	$\frac{1}{2}$ hour.	183	228	228
			1 hour.	179	228	228
			2 hours.	179	228	228
900° C.	5	1.60	$\frac{1}{2}$ hour.	444	340	340
			1 hour.	387	255	269
			2 hours.	332	228	228
1,060° C.	1	0.26	1 hour.	196	217	217
			2 hours.	192	217	217
			4 hours.	192	212	217
			8 hours.	183	202	217
1,060° C.	5	1.60	1 hour.	578	321	269
			2 hours.	495	277	255
			4 hours.	460	241	217
			8 hours.	351	223	217

These results show that whereas the low nickel steel was easily annealed in each experiment, the high nickel steel required a more prolonged soaking in order to anneal it. The results also show that the Ar.1 point in the high nickel steel probably occurs at a somewhat lower temperature than 700° C. even on very slow cooling.

With increasing content of nickel, the change austenite to pearlite occurs with still greater difficulty, such steels requiring a very slow rate of cooling in order to anneal them. Thus samples of steel containing 0.39 per cent. carbon, 10.5 per cent. chromium and 2.24 per cent. nickel, were reheated to 900° C. and 1,060° C., respectively, transferred to a second furnace maintained at 600° to 650° C. and, after soaking for different periods, were quenched out in water. They then gave the following Brinell hardness numbers :—

Soaked at 600/650° C.					Initial Temperature.	
					900° C.	1,060° C.
For 1 hour and W.Q.	477	555
For 2 hours	"	"	402	477
For 4	"	"	290	340
For 8	"	"	—	290
For 24	"	"	248	269
For 72	"	"	241	241

The samples soaked for 72 hours still contained a small amount of martensite after quenching.

Beyond the hardening effect noted with fully tempered steels, the presence of up to about two per cent. nickel does not appear to have any notable effect on the mechanical properties of stainless steel, at any rate with material of the carbon content mentioned below. Thus the tests given in Table XVIII were obtained on bars $1\frac{1}{4}$ inches diameter, and a comparison of the results on the two steels indicates that the high nickel steel has properties similar to those of that containing a small amount of nickel when the two steels are tempered to give the same tensile strength.

TABLE XVIII.

Influence of Nickel on the Mechanical Properties of Stainless Steel.

Steel.	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0.39	0.08	0.10	10.0	0.42
B.	0.39	0.12	0.32	10.5	2.24

Steel	Treatment.	Yield Point, tons per sq. inch	Maxi- mum Stress, tons per sq. inch	Elonga- tion % on 2 ins.	Reduc- tion of Area %	Brinell Hardness No.	Izod Impact, ft. lbs.
A.	O.H. 900° W.Q. 600° C.	49.0	64.2	15.0	45.9	302	22 19 20
	„ „ 650° C.	39.6	55.8	18.5	54.6	262	25 28 26
	„ „ 700° C.	31.2	49.6	24.5	58.6	235	75 66 72
B.	O.H. 900° W.Q. 600° C.	53.2	62.7	17.0	48.5	293	16 18
	„ „ 650° C.	46.4	59.0	20.0	52.2	277	30 29 26
	„ „ 700° C.	45.2	58.4	21.0	51.0	269	32 34 33

The high nickel steel mentioned above (as well as the corresponding steel with low nickel content) gave a Brinell hardness number of 555 to 600 when water quenched in the form of a thin disc from 1,200° C., that is, it remained completely martensitic. If the steel contains a somewhat larger amount of nickel, however, austenite is produced on

quenching from such high temperatures (i.e., $1,100^{\circ}$ or $1,200^{\circ}$ C.), though martensite is still formed on quenching from lower temperatures than these. Such steels, therefore, behave in a similar manner to the austenitic chromium steels, free from nickel, described on page 42. With still larger amounts of nickel, the temperature leading to the production of austenite is lowered, while the hardness produced on quenching from the temperature range giving martensite, diminishes. Finally, with sufficient nickel, the steel becomes entirely austenitic. The amount of nickel required to produce the several stages in the production of austenite varies with the amount of chromium present in the steel. According to Strauss and Maurer,* the amount required is shown in Fig. 65,

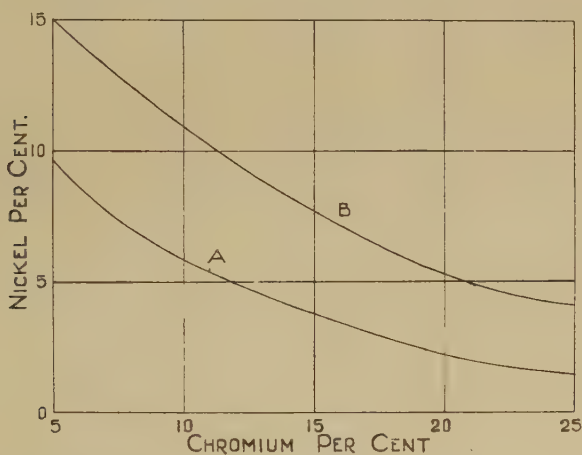


FIG. 65. Effect of nickel content on the production of austenite in high chromium steels (Strauss and Maurer).

in which curve A indicates the nickel content necessary to give austenite on quenching from high temperatures while a completely austenitic steel is obtained when the nickel content reaches that indicated by curve B. The author has found, however, that austenite is produced, on quenching from high temperatures, in steels containing distinctly less nickel than is indicated by curve A in Fig. 65.

The gradual change in properties as the nickel content is raised is well shown by plotting the Brinell hardness

* "Die Hochlegierten Chromnickelstähle als Nichtrostende Stähle." *Kruppsche Monatshefte*, Aug., 1920.

numbers obtained on quenching small samples of the steels from successively higher temperatures. Results obtained in this manner from steels containing, respectively,

		A	B
Carbon	0.45 %	0.28 %
Chromium	13.1 %	14.2 %
Nickel	2.54 %	4.96 %

are plotted in Figs. 66 and 67. The full lines, representing the results obtained on reheating samples which had previously been hardened by quenching from 950° C., indicate that the steels in this condition behave in a similar manner to those with lower nickel content. According to Strauss and Maurer's diagram (Fig. 65), steel A should not become austenitic while steel B is just on the limiting composition. Austenite was produced, however, on quenching both steels from high temperatures and the dotted lines in Figs. 66 and 67 show that on tempering these austenitic samples, they hardened in the same way as the austenitic chromium steels, previously described. The diagrams also show that as the nickel content increases, the austenite becomes more stable, requiring a higher temperature to break it down. This is further illustrated by curve A in Fig. 68, in which are plotted the results of a similar experiment on samples of a steel containing

Carbon	0.16 %
Chromium	13.7 %
Nickel	7.85 %

which had previously been made austenitic by quenching from 1,100° C. In this case the austenite does not break down until a temperature of about 750° C. is reached and there is no "tempering" range of the martensite so produced as in the steels illustrated in Figs. 66 and 67. Moreover, the hardness produced after reheating this steel in the range 850° to 900° C., and cooling therefrom, increases to some extent with the time of soaking in this range. If such hardened material is subsequently tempered, results similar to those shown in curve B, Fig. 68, are obtained. In this case the samples were first given a prolonged soaking in the range 850° to 900° C., and when cooled had a Brinell hardness number of 364. On subsequently reheating, they showed

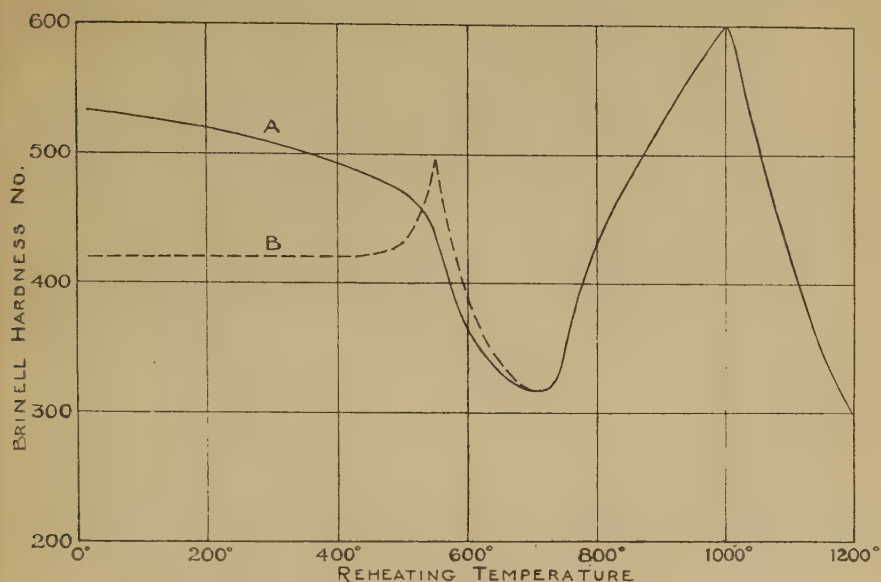


FIG. 66. Relation between Brinell hardness number and reheating temperature of steel containing 0.45 % carbon, 13.1 % chromium, 2.54 % nickel :—

Curve A. Samples previously W.H. 950°C.

Curve B. „ „ W.H. 1,100°C.

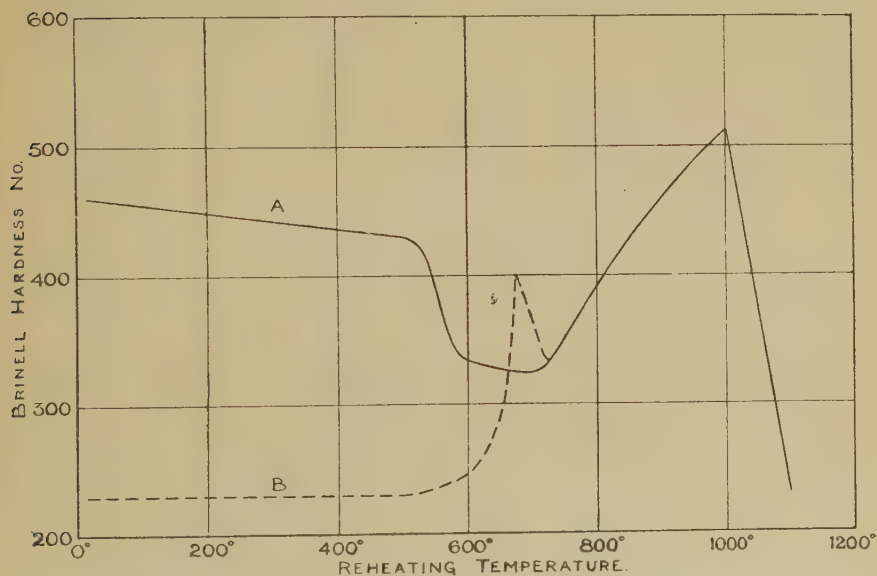


FIG. 67. Relation between Brinell hardness number and reheating temperature of steel containing 0.28 % carbon, 14.2 % chromium, and 4.96 % nickel.

Curve A. Samples previously W.H. 950°C.

Curve B. „ „ W.H. 1,100°C.

a tempering effect analogous to that of martensitic steels containing a smaller amount of nickel, as indicated in curve B. It is also interesting to note that the maximum tempering effect was obtained in the neighbourhood of 650°C ., and that the tempered steel began to harden again at a lower temperature than the austenitic form and also reached a greater hardness.

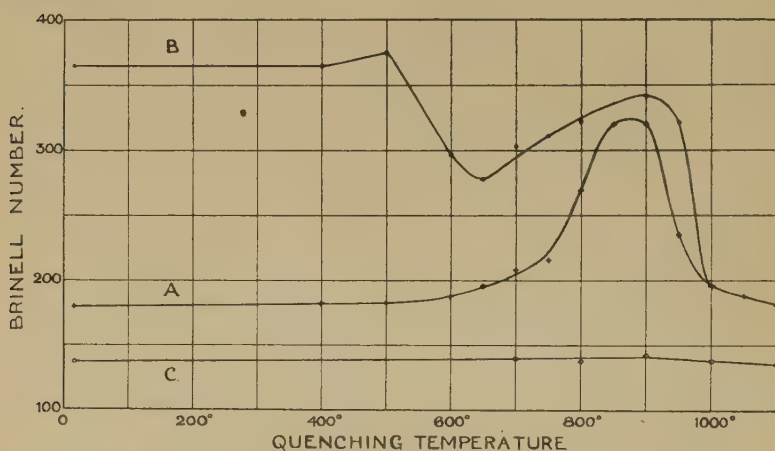


FIG. 68. Relation between Brinell Hardness number and reheating temperature of chromium nickel steels :—

Curve.	Carbon, %	Chromium, %	Nickel %	Previous Treatment.
A.	0.16	13.7	7.85	W.H. $1,100^{\circ}\text{C}$.
B.	0.16	13.7	7.85	Soaked $850/900^{\circ}\text{C}$.
C.	0.10	15.2	11.4	W.H. $1,000^{\circ}\text{C}$.

Steels containing a still greater amount of nickel remain completely austenitic after reheating to any temperature. Thus curve C, in Fig. 68, shows the Brinell hardness numbers obtained from steel containing :—

Carbon	0.10 %
Chromium	15.2 %
Nickel	11.4 %

after quenching from the temperatures indicated. A further account of these austenitic steels, which have some very valuable properties, will be given in Chapter VII.

(c) **Manganese.** The amount of this element present in stainless steel does not usually vary to any great extent.

Experiments were made, however, with two steels containing :—

		A	B
Carbon	0.26 %	0.26 %
Silicon	1.00 %	0.91 %
Manganese	1.33 %	2.08 %
Chromium	14.6 %	14.6 %
Nickel	0.33 %	0.33 %

to determine what effect, if any, the presence of manganese had on the hardening and tempering of stainless steel. The steels unfortunately contained more silicon than was desirable but it is possible to allow for the presence of this element in estimating the effect of the manganese.

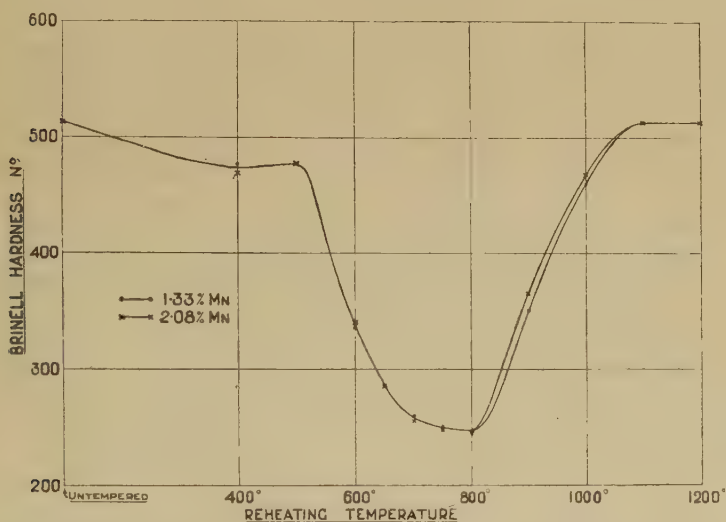


FIG. 69. Effect of manganese on the hardening and tempering of stainless steel.

Small samples of the two steels were hardened and then tempered at gradually increasing temperatures; the samples were quenched in water from each tempering heat and were then Brinelled. The results are plotted in Fig. 69. Bearing in mind the effect of one per cent. silicon in raising the temperature of the A_{c1} point about 50°C ., it would appear that manganese up to two per cent. has no great effect on the position of the carbon change point on heating, nor does it

modify to any appreciable extent the tempering of the hardened samples. In this respect it has a similar action, or lack of it, to that which it has on ordinary carbon steel. These results indicate that the presence of one or two per cent. manganese does not necessitate any modification in the heat treatment of the steel; mechanical tests on the bars showed no appreciable effect on the properties of the steel due to this manganese content.

These two steels showed no evidence of the production of austenite even when quenched from 1,200° C.; with a higher content of manganese, however, austenite is obtained, thus steels containing the following amounts of carbon, manganese and chromium:—

	A.	B.	C.	D.
Carbon % ...	0.70	1.08	0.43	0.53
Manganese % ...	3.2	5.1	5.3	6.7
Chromium % ...	14.1	14.9	14.8	12.8

were all austenitic when quenched from high temperatures, 1,000° C. to 1,200° C., though they were partly martensitic after reheating to and cooling from 800° to 1,000° C. They were also almost unmachineable.

(d) **Copper.** As a general rule this element is not present in any appreciable amount in stainless steel. As, however, certain claims, which will be discussed in the next chapter, have been made as to its effects on the resistance to corrosion of stainless steel, it is of interest to note its general effect on the hardening and tempering and also on the mechanical properties of the steel.

In curve A, Fig. 70, are plotted the Brinell hardness numbers obtained on tempering, at gradually increasing temperatures, samples of steel of the following analysis:—

Carbon	0.22 %
Silicon	0.28 %
Manganese	0.17 %
Chromium	12.1 %
Nickel	0.47 %
Copper	1.20 %

which had previously been air hardened from 950°C . From each tempering heat the samples were quenched in water. Curve B gives the results similarly obtained on a steel free from copper but otherwise identical in analysis, except that its carbon content was somewhat lower, 0.16 per cent. instead of 0.22 per cent. A comparison of the curves indicates that the presence of 1.20 per cent. copper lowers the Ac.1 point about 25°C ., a figure confirmed by thermal analysis. Allowing for the difference in carbon content of the two steels, it would also appear that copper increases slightly the hardness of the steel when the latter is tempered at 600°C . or above. The difference, however, is not great.

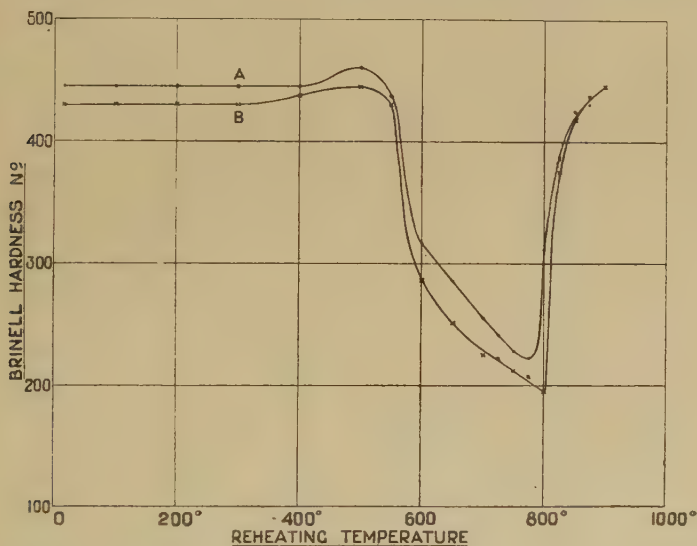


FIG. 70. Effect of copper on the hardening and tempering of stainless steel :—

Curve.	Carbon, %	Chromium, %	Copper, %
A.	0.22	12.1	1.20
B.	0.16	12.1	0.08

It would thus appear that copper acts in a somewhat similar manner to nickel but to a much less degree. The effect of about one per cent. copper is in fact so slight that its presence would not necessitate any modification of the ordinary methods of heat treatment of stainless steels.

On the other hand, the effect of copper differs from that of nickel in that the presence of fairly large amounts of the

former metal does not lead to the production of austenite. Thus samples of the following alloys :—

		A.	B.
Carbon	0·17 %	0·16 %
Silicon	0·33 %	0·33 %
Manganese	0·11 %	0·11 %
Chromium	14·0 %	15·7 %
Copper	5·0 %	9·85 %

were not austenitic when quenched from any temperature up to 1,200° C., the Brinell hardness numbers of small samples after water quenching from various temperatures being plotted in Fig. 71. It would also appear from these curves that the lowering of the temperature of Ac.1 which was noticeable with 1·2 per cent. copper does not become more pronounced with larger amounts of this element.

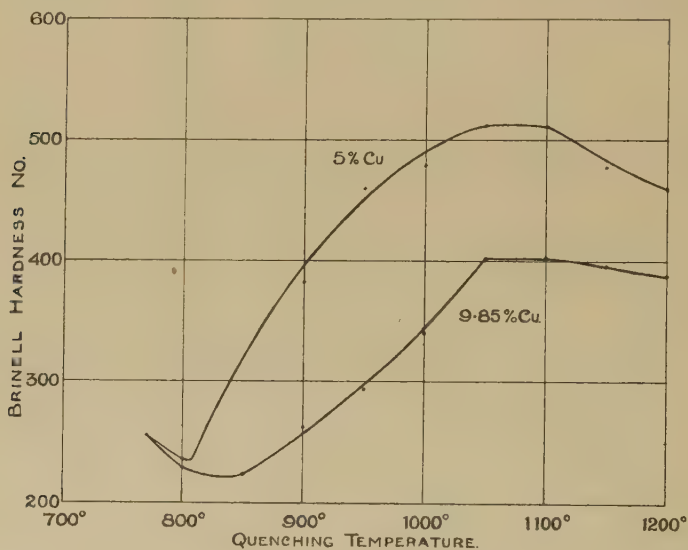


FIG. 71. Effect of high copper content on the hardening of stainless steel (see page 134 and compare with curve G. in Fig 51).

As the presence of small amounts of copper has occasionally been thought to exert a deleterious effect on the general properties of ordinary steel, it may be of interest

to note that the steel mentioned above, containing 1.2 per cent. copper, forged and rolled perfectly and that when hardened and tempered it was very tough; thus a bar, $1\frac{1}{8}$ inches diameter, after being air hardened from 950°C . and then tempered at 700°C ., gave a Brinell hardness number of 228 (corresponding to a tensile strength of 50 tons per square inch) and had an Izod impact value of 59 ft. lbs.

(e) **Aluminium.** This element is not usually present, except in minute amounts, in stainless steel. Occasionally, however, it may be found in appreciable quantity, more particularly in low carbon material which has been made by some type of the thermit process.

The effect of aluminium appears to be in many respects similar to that of silicon but in a much more pronounced degree. Like the latter element, aluminium raises very considerably the temperature of the Ac.1 point and, if present to the extent of about one per cent. or over, may prevent low carbon material from hardening in any great degree even when water quenched in the form

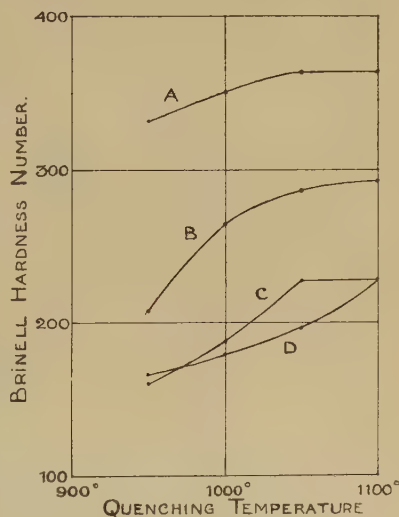


FIG. 72. Effect of aluminium on the hardening of stainless iron :—

Curve.	Carbon, %	Chromium, %	Aluminium, %
A.	0.09	12.0	0.15
B.	0.11	13.3	0.49
C.	0.11	10.9	1.08
D.	0.11	12.0	1.46

of small discs from any temperature up to $1,100^{\circ}\text{C}$. Such a non-hardening iron would have advantages from some points of view; unfortunately, however, such high aluminium material has a very low impact value, breaking under the impact test with a coarse crystalline fracture.

The effect of aluminium on the hardening of stainless material is shown in Figs. 72 and 73. In the former are plotted the Brinell hardness numbers obtained on quenching small discs, $\frac{1}{4}$ inch thick, of low carbon alloys of the following analyses :—

Curve	Carbon %	Silicon %	Manganese %	Chromium %	Aluminium %
A.	0.09	0.77	0.24	12.0	0.15
B.	0.11	0.64	0.20	13.3	0.49
C.	0.11	0.56	0.23	10.9	1.08
D.	0.11	0.58	0.20	12.0	1.46

A glance at these curves shows very plainly the effect of aluminium in raising the hardening temperature and also in preventing the metal hardening to any great extent.

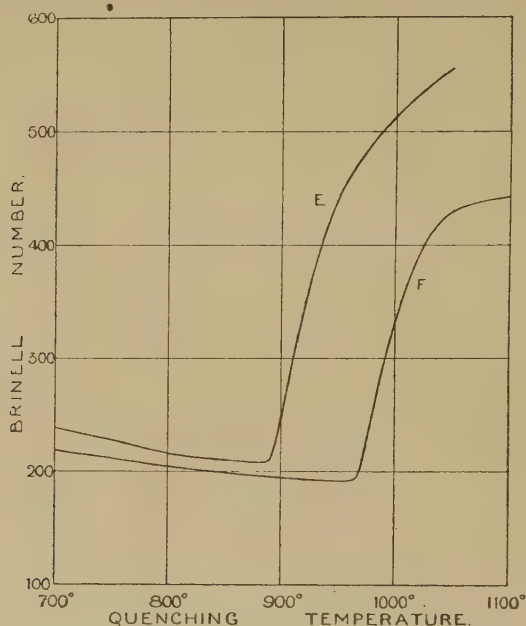


FIG. 73. Effect of aluminium on the hardening of stainless steel :—

Curve.	Carbon, %	Chromium, %	Aluminium, %
E.	0.26	12.4	0.62
F.	0.26	12.2	1.13

Fig. 73 gives the figures obtained from two steels containing :—

Curve	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %	Aluminium %
E.	0.26	0.68	0.20	12.4	0.45	0.62
F.	0.26	0.67	0.19	12.2	0.45	1.13

The samples were in the form of bars $\frac{5}{8}$ inch square and 2 inches long, and were quenched in water from the temperatures indicated. These curves indicate, after allowing for the silicon and nickel in the steel, that the presence of one per cent. aluminium raises the Ac.1 point about 120° C.

With regard to the impact value of these steels, samples E and F, when tested in the form of round bars, $1\frac{1}{8}$ inches diameter, gave the following results :—

Steel	Treatment.	Yield Point, tons per sq. in.	Max. Stress, tons per sq. in.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent	Brinell Hardness Number.		Izod Impact, ft. lbs.
						After Hard- ening	After Temp- ering	
E.	A.H. 1,000° W.Q. 700° C. ...	46.0	56.0	16.0	47.2	337	248	18 23
F.	A.H. 1,050° W.Q. 700° C. ...	39.2	53.8	17.0	40.6	340	255	12 10 10

All the impact fractures were coarsely crystalline. The values for elongation and reduction of area in the tensile test are also not particularly good.

Similar impact results were obtained from the low carbon steels. Steel A (page 136) when oil hardened from 1,000° C. and tempered at 700° C. (in the form of a round bar, 1 inch diameter) gave the following mechanical test :—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hardness Number		Izod Impact, ft. lbs.
				After Hard- ening.	After Temp- ering.	
35.2	42.6	30.0	67.8	321	207	104 105 102

a result, of course, typical of tough ductile material such as stainless iron should be. Samples B to D, on the other hand, when water hardened and tempered, in the form of $\frac{1}{2}$ inch square bars, gave the values indicated below :—

Steel.	Treatment.	Brinell Hardness Number		Izod Impact, ft. lbs.
		After Hardening.	After Tempering.	
B.	W.H. 950° W.Q. 700° C	212	166	12 14
B.	W.H. 1,050° W.Q. 700° C.	235	179	15 20
C.	W.H. 1,050° W.Q. 700° C.	207	174	10 11
D.	W.H. 1,050° W.Q. 700° C.	207	187	10 11

All the samples were coarsely crystalline, the coarseness being particularly evident in samples C and D, nor was it found possible to improve the appearance of the fractures by any treatment up to a temperature of $1,100^{\circ}\text{C}$.

The Influence of Cold Work on the Mechanical Properties of Stainless Steel. Stainless steels may be cold worked in the same way as ordinary steel; thus they may be drawn into wire, rolled into sheets or strip, made into weldless drawn tubes, or pressed or stamped into a variety of shapes. They are, however, more difficult to work than ordinary carbon steels and require softening more frequently between the successive stages in the drawing, rolling, stamping or pressing operations. It is also necessary to modify to some extent the usual operations in producing the various types of worked products mentioned above. The lower carbon stainless steels, particularly stainless iron, owing to their greater softness, are better adapted for cold working operations than those of higher carbon content.

In wire drawing, the stainless material, as a rule, requires softening (or "annealing" as it is generally called in the trade) every one or two passes. Owing to this, cold drawn stainless wire is not generally produced with such a high tensile strength as is possible with carbon steel wire because, for the production of such high tensile strength, it is necessary that the wire be given a number of successive reductions without any intermediate annealing, a procedure presenting no great difficulty with ordinary carbon steel.

To soften the material, whether it be in the form of wire rod, hot rolled sheet, hot rolled tube, or the same materials more or less cold worked, it should be reheated to $700^{\circ}/750^{\circ}\text{C}$. and may then be cooled slowly or quenched, as may be convenient. The scale produced by any previous hot working may be removed by pickling as described earlier. During the intermediate softenings at 700° to 750°C . of the cold worked material between successive stages in the cold working operation, only a slight tarnish is produced on the metallic surface of the cold worked article and further pickling may not be necessary even though the method of "close annealing" has not been used.

It is not possible to "patent" stainless wire before proceeding to draw it as is done with ordinary carbon steels. Stainless steel has notable air hardening properties and air

cooling from the temperature at which "patenting" is carried out would leave the wire rod hard and somewhat brittle.

From a corrosion resisting point of view, it is undesirable to put into service an article in a drastically cold worked condition; it should be hardened and tempered after the cold-working operation. This may limit the use of stainless steel for certain purposes but it should be borne in mind that the hardening does not necessarily involve any quenching in oil or water; air cooling is generally quite sufficient.

For most purposes for which a bright drawn or cold rolled surface is required, the best procedure is to harden and temper and then pickle the material before the last pass through the die or rolls. If the amount of reduction at this last pass is suitably chosen, the finished material will then have a bright surface and being only slightly cold worked will have good resistance to corrosion.

Still better results are obtained, especially with wire, if the surface is finally ground and polished after the last pass.

Experiments in the softening of heavily cold drawn stainless iron wire show that distinct softening occurs at a temperature of 500°C . and further reduction in tensile strength and hardness at 600° and 700°C . Thus the results given in Table XIX were obtained from wire of the following analysis:—

Carbon	0.07 %
Silicon	0.08 %
Manganese	0.12 %
Chromium	11.7 %
Nickel	0.57 %

which had been drawn from 5-gauge rod.

TABLE XIX.

Tests on Hard Drawn Stainless Iron Wire.

Gauge.	Diameter, inches.	As Drawn.		Tempered 500°C .		Tempered 600°C .		Tempered 700°C .	
		Max. Stress, tons per sq. inch.	Reverse Bend Test.	Max. Stress, tons per sq. inch.	Reverse Bend Test.	Max. Stress, tons per sq. inch.	Reverse Bend Test.	Max. Stress, tons per sq. inch.	Reverse Bend Test.
11	.111	68	5	59.5	6	46	8	36	9
14	.0804	78	5	64.5	$7\frac{1}{2}$	50	$16\frac{1}{2}$	39.5	15
15	.0706	89	5	61	9	49	18	38	18
17	.0568	114	4	67	$11\frac{1}{2}$	50.5	20	40.5	27
18	.0465	103	13	61	22	46	30	39	41

The reverse bend test was carried out by fixing the sample in a vice which had the inner edges of the jaws rounded to a radius of 5 mm. The projecting end of the wire was then bent at right-angles to the fixed part, first to one side then to the other, until it broke. The number of bends through 180° was noted, the first bend through 90° not being counted.

The material used for this wire was the same as that used for the series of tests given in Table I (page 81) and Fig. 46; it is interesting to note the similarity in tensile strength between the cold worked samples and those oil hardened, after both had been tempered at the same temperatures. It would also appear from the results given in Table XIX that the tensile strength of the cold drawn wire is reduced to about 60 to 65 tons per square inch, on tempering at 500°C. , no matter what its strength was before tempering, providing, of course, that the strength, as drawn, exceeded the range mentioned.

Wire which has been given only one or two draws after the final hardening and tempering operation will have a tensile strength which will be only a few tons per square inch higher than that produced in the wire as a result of this hardening and tempering. Hence the tensile strength of the finished wire will obviously depend largely on this heat treatment. Probably the tensile strength of such wire will, in general, be between about 40 and 80 tons per square inch.

A study of the effect of low temperature annealing on cold drawn stainless iron and steel rods was recently published by S. H. Rees.* The material was in the form of rods, $\frac{3}{4}$ inch diameter, which were commercially described as "cold drawn, ground and polished," and had the following analyses:—

		Stainless Iron.	Stainless Steel.
Carbon	...	0.12 %	0.40 %
Silicon	...	0.16 %	0.52 %
Manganese	...	0.13 %	0.24 %
Chromium	...	12.0 %	13.0 %
Nickel	...	0.25 %	0.06 %

Both tensile and compression tests were carried out with the results given in Table XX.

* "Effect of Low Temperature Annealing on Some Mechanical Properties of Cold Drawn Steels." *J.I.S.I.*, 1923, II, p. 273.

TABLE XX.

*Properties of Cold Drawn Stainless Steels after
Annealing at Low Temperatures.*

Treatment.	Tensile Test.					Compression Test.	
	Elastic Limit, tons per sq. inch.	Yield Point, tons per sq. inch.	Max. Stress, tons per sq. inch.	Elongation per cent. on 2 ins.	Reduction of Area per cent.	Elastic Limit, tons per sq. inch.	Yield Point, tons per sq. inch.
STAINLESS IRON—							
Cold drawn, as received	7	32	37.2	28.5	70	9	28
Ann. 1 hour at 100° C.	8	32	37.2	28	70	9	28
„ „ 200° C.	14	32.5	37.6	27	70	12	27
„ „ 300° C.	22	33	38.0	24	69	18	30
„ „ 375° C.	22	26	34.0	32	73	20	26
„ „ 450° C.	19	26	34.0	32	72	19	26
„ „ 650° C.	18	20	32.8	37	74	16	21
STAINLESS STEEL—							
Cold drawn, as received	9	39	50.8	21	50	7	35
Ann. 1 hour at 100° C.	10	39	50.8	21	52	10	34
„ „ 200° C.	17	40	51.2	19	50	17	36
„ „ 300° C.	24	43	50.8	20	52	22	37
„ „ 375° C.	29	40	50.4	21	52	26	35.5
„ „ 450° C.	28	39	50.4	22	53	25	35
„ „ 550° C.	26	35	49.2	22.5	55	26	33.5
„ „ 650° C.	24	32	48.4	25	57	23	32.5
„ „ 780° C.	24	31	47.6	26	57	25	31.5

As will be seen, the effect of an annealing at 300° to 375° C., in the case of the stainless iron, or 375° to 450° C., in the case of the steel, results in a very marked improvement of the elastic properties of the cold drawn rods. In this respect stainless material behaves in a similar manner to carbon steels.

In the production of pressings from stainless iron sheet or strip, a considerable saving in the cost of grinding and polishing may be obtained by taking advantage of the fact that the thin film of oxide produced in the softening of the pressing (by heating to 700°/750° C.) between the successive stages of the pressing operation, is readily removed by suitable pickling, leaving a surface capable of being easily polished. The sheet should be ground prior to pressing,

the grinding of a flat surface being considerably cheaper than that of the more intricate surface of a pressing ; if the oxide film produced by the intermediate annealings is then removed by the special pickle described on page 68 (containing nitric and hydrochloric acids), the silvery grey surface so produced will be found to take a polish quite easily, particularly as the final pressing operation itself will brighten the surface considerably. This method may also be used if, owing to very severe local deformation, it is thought advisable to harden and temper before the final pressing operation. If such hardening and tempering is carried out with care, the scale which forms* on the smooth surface of the ground and partly pressed sheet is removed very easily by the pickle mentioned above so that, after the article had been finally pressed, only a short buffing operation is necessary to polish the surface.

Some Physical Properties of Stainless Steel. The following data regarding some of the physical properties of stainless material may be of interest.

Density. The metal chromium is lighter than iron and hence its addition to steel lowers the density of the latter. The actual value of the density will obviously depend on the amount of chromium present in the steel ; it is also affected, as with ordinary carbon steels, by the amount of carbon in the steel. Also, the density of any particular steel varies slightly with the heat treatment to which it has been subjected, the stainless steel again being affected in a similar manner to ordinary carbon steel, that is, its density is somewhat lower in the hardened condition than in the hardened and fully tempered or the annealed conditions. As an indication of the average values, the following figures may be quoted :—

- (a) Effect of heat treatment—steel with 0·3 per cent. carbon and 12·6 per cent. chromium.

A.H. 950° C.	7·731
A.H. 950° C., T. 700° C.	7·738

- (b) Effect of varying carbon and chromium—all samples hardened and fully tempered. —

Mild Steel	7·869
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Stainless Steel—

0·3 % carbon ; 10·6 % chromium ... 7·751

0·3 % carbon ; 12·6 % chromium ... 7·738

Stainless Iron—

0·08 % carbon ; 12·3 % chromium ... 7·779

0·08 % carbon ; 15·4 % chromium ... 7·722

0·10 % carbon ; 20·4 % chromium ... 7·683

Co-efficient of Expansion. Stainless steel expands somewhat more slowly with increase in temperature than ordinary mild steel and distinctly more slowly than copper and the ordinary copper alloys ; possibly the most accurate data available for the expansion of stainless steel are those obtained at the Bureau of Standards (U.S.A.)* where the values given in Table XXI were found for steel containing : —

Carbon	0·30 %
Silicon	0·11 %
Manganese	0·18 %
Chromium	13·1 %

Determinations were made on the steel in the hardened condition and also after tempering at 760° C. (this is referred to in the original as “annealing” ; as, however, 760° C. is below the Ac.1 range of the steel, such an “annealing” is in the nature of a tempering operation).

TABLE XXI.

Co-efficient of Expansion of Stainless Steel.

Temperature Range.	Average Co-efficient of Expansion.	
	Hardened.	Tempered.
20° to 100° C.	$9·9 \times 10^{-6}$	$10·3 \times 10^{-6}$
20° to 200° C.	$9·8 \times 10^{-6}$	$10·7 \times 10^{-6}$
200° to 400° C.	$9·9 \times 10^{-6}$	$12·2 \times 10^{-6}$
400° to 600° C.	$13·8 \times 10^{-6}$	$13·3 \times 10^{-6}$
600° to 800° C.	$13·4 \times 10^{-6}$	$13·6 \times 10^{-6}$
20° to 600° C.	$11·2 \times 10^{-6}$	$12·1 \times 10^{-6}$

* Bureau of Standards, Scientific Paper No. 426.

Taking these figures and the usually accepted data for mild steel, copper, aluminium, monel metal, brass and bronze, the total expansion at various temperatures of bars 10 inches long, of these metals, is represented in Fig. 74.

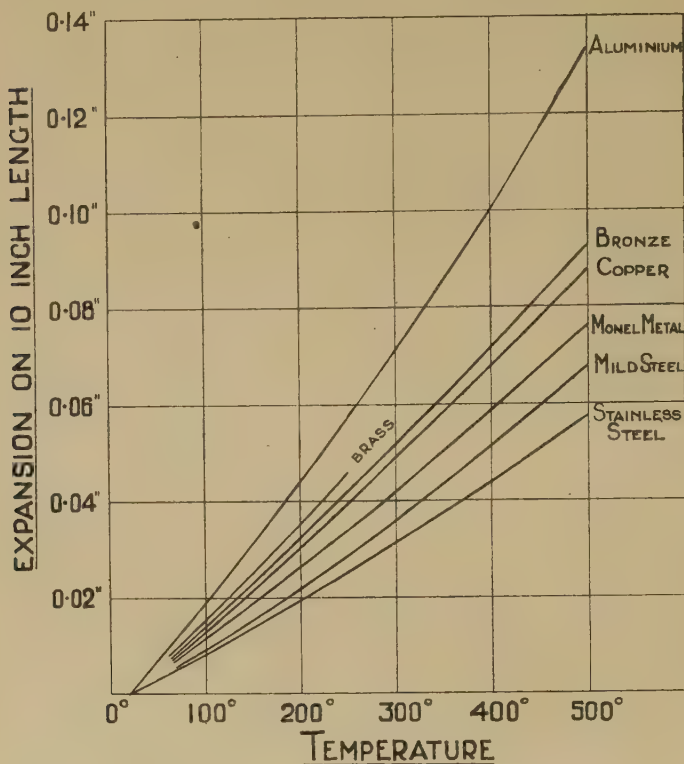


FIG. 74. Total expansion at temperatures up to 500°C. of rods 10-ins. long (at 20°C.) of various metals and alloys.

The importance of the value of the co-efficient of expansion in the case of metals used for steam and other fittings working at temperatures above normal is obvious. Owing to the comparatively low value of this co-efficient for stainless steel, parts made from this material which work inside others made of copper alloys are not likely to become tight and seize when both become hot.

Thermal Conductivity. Results have been published* by Dr. Hatfield, indicating that stainless steel has

* Dr. W. H. Hatfield; "Stainless Steels." *Coventry Engineering Society Journal*, June, 1923.

a lower thermal conductivity than ordinary mild steel. He gives a range for stainless steel of 0.0363 to 0.0466 c.g.s. units, while published values for iron give 0.1450 c.g.s. units, and, for mild steel, 0.1436 c.g. units at 18° C., and 0.1420 c.g.s. units at 100° C.,* respectively. These values would indicate a considerably slower conduction of heat in stainless material than in ordinary mild steel. A question however, which is of considerable importance to users of stainless steel is its rate of heating, compared with that of ordinary steel, when both are heated under similar conditions in furnaces. The rate of heating of a metal depends on its thermal diffusivity and this varies directly as the conductivity and inversely as the thermal capacity of unit volume of the metal, i.e.,

$$\text{Diffusivity} = \frac{K}{S \times D}$$

where K = thermal conductivity.

S = specific heat.

D = density.

The comparatively low value for the thermal conductivity of stainless steel would suggest, therefore, that this material would heat up considerably slower than ordinary carbon steel, when both are placed in a furnace under identical conditions, unless the specific heats of the two vary widely. Actually, however, no such great difference in the rate of heating is observable. Experiments were carried out in which bars of stainless steel (0.22 per cent. carbon, 0.25 per cent. silicon, 0.15 per cent. manganese, 13.6 per cent. chromium), and of ordinary carbon steel (0.41 per cent. carbon, 0.20 per cent. silicon, 0.73 per cent. manganese) were heated up both in a salt bath and in a gas fired furnace, and the rates of heating of the two samples determined. For this purpose each of the bars, which were $1\frac{7}{8}$ inches in diameter and 12 inches long, was bored longitudinally along its axis with a hole, $\frac{5}{16}$ inch diameter, for a distance of six inches from one end, and thermocouples inserted into these holes. Continuous records of the rise in temperature of these thermocouples were taken on a Brearley

* Jaeger & Diesselhorst: Landolt-Bornstein, Physikalisch-Chemische Tabellen, p. 737.

curve tracer. By this means, the time at which any temperature was reached by the bars could be read to about five seconds.

In the case of the experiments with the salt bath, the latter had a melting point of 180°C ., and the pieces were immersed for a depth of 10 inches. The bath was allowed to reach a temperature of 580°C . and become steady before each experiment. Two sets of experiments were carried out, the results of which are plotted in Fig. 75. It will be seen that the rates of heating of the two steels were identical within the limits of experimental error.

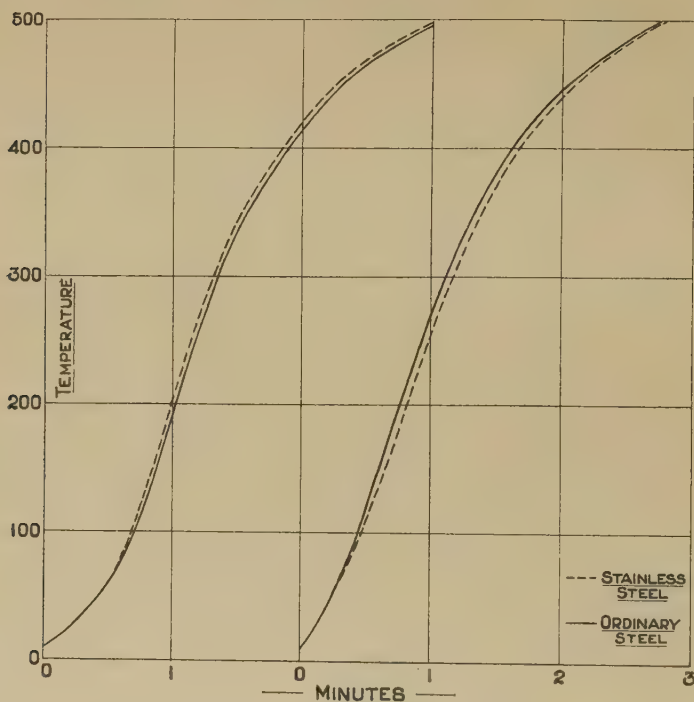


FIG. 75. Rates of heating, in a salt bath, of similar bars of mild steel and stainless steel.

Precisely similar results were obtained on heating the bars in a gas fired furnace previously heated to 700°C . In this case, the rate of heating was naturally much slower than with the salt bath, but again the two steels increased in temperature at substantially the same rate.

In comparing these results with the values for thermal conductivity given on page 145 it may be mentioned that the latter were taken over a limited range of temperature only slightly above atmospheric and that the value of the thermal conductivity may, and probably does, alter with rise in temperature. There does not seem to be any reason to suppose that the specific heat of stainless steel differs materially from that of ordinary steel. So far as the author is aware, no determinations of the specific heat at various temperatures of such high chromium steels have been made. At ordinary temperatures Brown* found a value of 0.1206 for a steel containing 1.09 per cent. carbon and 9.50 per cent. chromium, while Dr. Hatfield (in the paper previously quoted) gives values of 0.115 to 0.121 for stainless steel at ordinary temperatures. These values are practically the same as that of ordinary steel.

Electrical Resistance. The electrical resistance of stainless steel varies with its composition and with the heat treatment to which it has been submitted. For any given steel, the resistance is lowest in the annealed condition and highest when hardened from high temperatures. The gradual increase in resistance obtained by quenching a high chromium steel such as stainless, from gradually increasing temperatures above the A_{c1} point, was shown by Edwards and Norbury,† and their curves indicate that this increase in resistance takes place over the range of temperature in which the carbide of the pearlite gradually dissolves (see Chapter II, p. 29).

In the annealed or fully-tempered condition, stainless steel has a resistivity of about 0.00005 to 0.000055 ohms per c.m.³; this increases to about 0.00007 when the steel is quenched from temperatures high enough to dissolve the whole of the carbide. On tempering the hardened steel, the electrical resistance falls in a similar manner to the Brinell hardness number.

The value of the resistivity is raised by the presence of silicon or other metals which enter into solid solution in the steel. It also rises with increasing chromium content.

* Landolt-Bornstein, *Physikalisch-Chemische Tabellen*, p. 751.

† "Chromium Steels: Effect of Heat Treatment on Electrical Resistivity." *J.I.S.I.*, 1920, I, p. 447.

The effect may be seen by comparing the resistivity of two low carbon steels of the following analyses :—

		A	B
Carbon	0·07 %	0·13 %
Silicon	0·08 %	0·90 %
Manganese	0·12 %	0·27 %
Chromium	11·7 %	17·5 %
Nickel	0·57 %	0·78 %

the former had a value, when fully tempered, of 0·0000513, the latter of 0·0000744 ohms per cm.³.

Magnetic Properties. Stainless steel has magnetic properties of the same type as those of a high carbon steel. It makes, when suitably hardened, a very good permanent magnet, being considerably superior in this respect to high carbon steel, though inferior to the ordinary six per cent. tungsten steel generally used for magnets. Where its rust resisting properties would be of considerable moment, it would probably find valuable application as a magnet steel.

INFLUENCE OF VARYING TREATMENT AND
COMPOSITION ON THE RESISTANCE TO
CORROSION OF STAINLESS STEEL

CHAPTER V

INFLUENCE OF VARYING TREATMENT AND COMPOSITION ON THE RESISTANCE TO CORROSION OF STAINLESS STEEL

The subject of the corrosion of iron and its alloys is extremely complex; a great deal of experimental work has been carried out, there are numerous papers bearing on the subject to be found in scientific and technical literature and several theories have been propounded to explain the experimental results, often of an apparently contradictory nature, which have been obtained by various workers. Until quite recently, the two most important theories with respect to the corrosion of iron were the "acid" and "electrochemical" theories. The former theory regarded the presence of, at any rate a minute proportion of, some acid as necessary in order that corrosion could take place while the latter held that the small physical and chemical variations present in samples of even the purest metals obtainable set up electrochemical effects which would cause corrosion to take place in the absence of any free acids. Neither theory satisfactorily explained all the phenomena of the corrosion of iron, however, and hence special theories have been developed during recent years to account for the observed results. Some of these theories depend on chemical attributes of iron which are not possessed by other metals and, as they obviously do not apply to these, they tend to complicate matters.

Investigations carried out recently by U. R. Evans,* following on the work of Aston,† have served, however, to reconcile some of the conflicting statements and evolve some order in the theories of corrosion. According to Evans, corrosion is electrochemical in character, but his

* Evans: *J. Inst. Metals*, Vol. 30, p. 239. *Trans. Faraday Society*, Vol. 18, p. 1; Vol. 19, pp. 201 and 789, and other papers. See also the recently published book, "The Corrosion of Metals," by the same author.

† J. Aston: *Trans. Amer. Electrochem. Soc.*, Vol. 29 (1916), p. 449.

theory differs from the older one in that he believes the potential differences set up in different parts of a sample, which cause the corrosion, are due not only to variations in the metal itself but also in the corroding fluid surrounding it. The effect of variations in the fluid may be illustrated by the action of the small amount of dissolved oxygen which is always present in ordinary water. If a sample of ordinary steel sheet is immersed in a large tank of water, the amount of dissolved oxygen which the water contains will very probably soon vary from place to place in the tank, even though the water was well mixed up at first. Evans' work has shown conclusively that, in such a case, electrochemical action is set up as a result of this difference in oxygen concentration and that when this happens, the part of the steel sheet in contact with the water containing least oxygen in solution acts as the anode and is, therefore, attacked at a faster rate than the part bathed by the water with high oxygen content which functions as cathode. This result is extremely important as it offers the first convincing explanation of the known fact that excessive corrosion is often produced at places where oxygen has the least access, such places, for example, as pits or grooves, or under dirt or debris, including products of corrosion, which may have settled on part of the surface of the metal. It may also be the cause of the tendency which stainless steel has been observed to possess of undergoing slight corrosion at the point where it is supported when it is exposed to some solutions.

The author has no desire, however, to enter into a detailed discussion of the present state of the theories of corrosion; it would be outside the scope of this book.* Suffice it to say that though much headway has been made, notably as a result of the work of Evans, Friend, Bengough, Vernon and others, very much remains to be elucidated. Before considering the particular problem of the resistance to corrosion of stainless steel, it may be well, however, to consider briefly one or two fundamental facts with regard to the corrosion of iron.

Whether a sample of absolutely pure iron, which was

* To those interested, the author would especially recommend a study of "The Corrosion of Metals" by U. R. Evans (Arnold, London, 1924). The experimental work of Dr. Friend, mainly published in the *Journal of the Iron and Steel Institute*, should also be consulted.

physically uniform in every part, would corrode if immersed in absolutely pure water may be a matter of doubt; there can be no doubt, however, that the purest iron commercially available will corrode in ordinary distilled water or in ordinary drinking water. There is also no doubt that, on corrosion taking place, the iron goes into solution in the water and is subsequently precipitated from this solution as a hydroxide, either at or near the spot where it dissolved or after diffusing an appreciable distance through the water. Secondly, the less homogeneous, either physically or chemically or both, a sample of iron is, the greater, as a general rule, is its tendency to corrode. Thus the addition of carbon to iron produces a carbide which may exist as separate particles more or less unevenly distributed through the mass of the metal. This carbide of iron is electronegative to iron and hence tends to increase the rate of corrosion of the latter. A study of the microstructure of ordinary steels shows that these, under different conditions of heat treatment, may be either homogeneous or heterogeneous and this to a varying degree. Their rate of corrosion under such differing conditions also varies.

Applying these two fundamentals to the special problem of stainless material, it is evident in the first place that the presence of sufficient chromium in solid solution in iron reduces the solubility of this metal in water practically to zero. It is not known why the addition of suitable amounts of chromium to iron should have this effect; it seems possible, however, that it may be due partly to what is known as "passivity." It is common knowledge that iron or ordinary steel is readily attacked by nitric acid so long as the strength of the acid does not exceed that corresponding to a specific gravity of about 1.25. With somewhat stronger acid than this, e.g., corresponding to a specific gravity of 1.3 or 1.35, these metals are attacked when first immersed in the acid, but after an interval, the rate of attack falls off markedly and may cease altogether. With still stronger acid, e.g., the concentrated form as ordinarily sold and having a specific gravity of 1.42, no attack appears to take place at all, or as it is generally said, in such an acid the metal becomes "passive." Iron which has been made passive by the action of strong nitric acid retains, for a longer or shorter period after being taken out of the acid, certain peculiarities in its behaviour

to other reagents. Thus it is not immediately attacked by nitric acid of specific gravity 1.20 nor will it precipitate copper from solutions of salts of this metal in the manner that iron does normally. In other words, the passive iron has a greater resistance to the attack of certain reagents than has the normal metal. Such a passive condition may be produced in iron by the action of other reagents, generally of an oxidising nature, or by electrochemical means. The passivity produced in iron by any such means is more or less transient; although the passive metal resists for a short period other reagents, which do not themselves produce passivity in the metal, such resistance is only temporary and at the end of a longer or shorter time, the metal is attacked. The metal chromium exhibits passivity effects in a much more pronounced manner than iron and also under the influence of reagents which do not produce passivity in iron. Hence it is reasonable to suppose that chromium, when added to iron, greatly increases the tendency to passivity already present in this metal.

The cause of passivity is not definitely known but it seems very probable that the surface of the passive metal is covered with a layer, possibly only one or two molecules thick, of an oxide of the metal, further action being prevented by this film. Such an excessively thin film is, of course, entirely beyond the sensitiveness of any chemical methods of analysis which one could use to indicate its presence. Some account of passivity effects in connection with the attack of certain acids on stainless steel will be given later.

When chromium is added in small quantities to steel, it appears at first to be associated entirely with the carbon in the steel. Afterwards, as the amount of chromium is increased, part of it is present in solid solution in the iron, the amount in solution, for any given chromium content, depending on the amount of carbon in the steel.

The composition of the carbide normally present in stainless steel has not been accurately determined; there is some doubt, in fact, as to whether it has a constant composition, there being evidence to show that the ratio of iron, chromium and carbon in the carbide may vary to some extent under different conditions of heat treatment. As an approximate figure for its average value, however, the ratio of chromium to carbon in the carbide may be taken as

ten to one. It is obvious, therefore, that the amount of carbon present in the steel has a very decided influence on the amount of chromium available for inducing incorrodibility in the iron and also that the physical condition of the carbide present in any one steel will affect the degree of resistance to corrosion of that steel. In this chapter it is intended to indicate firstly, how the degree of resistance in any one sample of stainless steel is affected by variations in heat treatment to which it may be subjected and, secondly, the general effect of alterations in composition on the resistance to corrosion of stainless steels.

From the general principle that heterogeneity tends to increase the rate of attack of steel by different corroding media, we should expect to find, and actually do find, that the greatest resistance to corrosion of any one steel is obtained after quenching it in such a manner that it consists entirely of martensite, while the least resistant form is obtained on annealing the steel so as to produce a complete separation of carbide and ferrite. In the former case, all the chromium (as well as the carbon) is in solution in the iron and therefore the full effect of the whole of the chromium present is obtained; in the latter case, not only does the separation of carbide tend to decrease the resistance to corrosion owing to galvanic effects but, in addition, it lowers the concentration of the chromium in solution in the iron because the carbide which separates out contains a large amount of chromium. Hence the body of the steel possesses a less resistance to corrosion than when it contained the whole of the chromium in solution.

With any given steel, therefore, the effect of variation in heat treatment may be summarised as follows:—

Hardening. The greatest resistance to corrosion will be obtained by quenching the steel from a temperature sufficiently high to dissolve all the carbide which it contains. In practice, however, it is found that quenching a steel of normal composition from a temperature of 900°C. to 950°C. produces a material which is practically insoluble in water and certain other media, such as vinegar and fruit juices, and that increasing the hardening temperature beyond this range produces no marked improvement while, on the other hand, it seriously increases the risk of cracking during hardening. In the case of samples which have subsequently

to be tempered almost completely there would appear to be no advantage whatever, from the point of view of resistance to corrosion, in raising the quenching temperature sufficiently high to take into solution the remnants of the carbide left undissolved at 900° to 950° C., because the whole of the dissolved carbide will be thrown out of solution again in the subsequent tempering operation. In this case, the quenching temperature should be selected to give the best mechanical properties in the manner described in the last chapter.

The effect of raising the quenching temperature on the resistance to corrosion of quenched samples may, however, be illustrated by using steels with a lower chromium content than that present in stainless steels, such steels being more susceptible to the influence of heat treatment than normal stainless steels. For example, samples of steel which had the following analysis :—

Carbon	0.53 %
Silicon	0.73 %
Manganese	0.21 %
Chromium	8.60 %

and was, therefore, considerably outside the range of composition used for stainless material, were quenched from the following temperatures :

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.
Temperature ...	950° C.	$1,000^{\circ}$ C.	$1,050^{\circ}$ C.	$1,120^{\circ}$ C.	$1,200^{\circ}$ C.

After quenching, No. 1 contained a considerable amount of free carbide, No. 2 less, No. 3 only traces, whilst Nos. 4 and 5 consisted entirely of martensite. The pieces were ground and polished, and then tested by placing a small drop of vinegar on each polished surface and allowing it to dry gradually.* The dry residues from the drops were then washed off in water. Sample No. 1 was then found to be

* This spot test with vinegar is regularly used in testing material for cutlery. It is a more severe test than placing the sample for 12 or 24 hours in vinegar.

decidedly stained by the vinegar test, No. 2 less so, No. 3 only slightly, while Nos. 4 and 5 were unattacked. This indicates very clearly that the resistance of the material to staining increases with the quenching temperature and with the progressive solution of the carbide which takes place as the temperature rises.

Tempering. From the fact that no appreciable loss of hardness is produced on tempering hardened samples of stainless steel up to about 500°C. , and that after such tempering the structure of a previously quenched sample is still martensitic, it would not be expected that such a tempering would have any great effect on the resistance to corrosion of the hardened material, nor has any such effect been found. This fact is of great importance commercially, as such a tempering removes to a very great extent the internal stresses set up during hardening and also improves considerably the ductility and toughness of the material, as was shown in the last chapter.

The sudden and marked fall in hardness which is produced as the tempering temperature rises from 500° to 600°C. , is accompanied by a lessened resistance to corrosion of the material. Such softened material, for example, may stain when tested with vinegar as described earlier, but even in this condition it is attacked extremely slowly. Whether it will actually stain or not with the vinegar test depends on the amount of carbon and chromium it contains. As probably the greater part, if not all, of the carbide is thrown out of solution by tempering at 600°C. and the chief effect of tempering at higher temperatures than this consists in the coalescence of the small carbide particles already present into larger, it would not be expected that there would be any marked difference in the resistance to corrosion of samples tempered at 600°C. and of those tempered at higher temperatures, e.g., 700° to 750°C. On theoretical grounds there are probably two opposing effects produced by the higher tempering range :—

(a) A further small precipitation of carbide resulting in a diminution of the concentration of dissolved chromium and hence tending to produce a lessened resistance to attack.

(b) The coalescence of the carbide particles causes

a very decided decrease in the total surface area of the latter. It is reasonable to suppose that this diminution of surface will tend to reduce any galvanic effect between the carbide and the ferrite and hence tend to increase the resistance to attack.

It is quite possible that these opposing effects may have different relative values with different corroding media and that using the same set of samples, tests with some reagents will show that tempering at a higher temperature than 600° C. slightly reduces the resistance while, with other media, the same softer samples will be somewhat less corrodible than the harder pieces. As an example of the differing effects of varying reagents on samples tempered at different temperatures, the following figures may be quoted.

Polished samples of steel of the following composition :—

Carbon	0·34 %
Silicon	0·13 %
Manganese	0·26 %
Chromium	11·6 %

which had been hardened and then tempered at various temperatures, were placed for 21 days in pure malt vinegar, containing 5 per cent. acetic acid. At the end of that period the pieces which had been tempered at temperatures up to 500° C. showed no signs of attack. Samples tempered at 550° and 600° C. had been slightly but distinctly attacked, producing an etched appearance on the polished surface. The losses in weight were 0·26 and 0·19 milligrams per square cm. of surface. The sample tempered at 700° C. was obviously less attacked; it showed the etching effect less distinctly, and the loss in weight was only half to one-third of the preceding figures, viz., 0·08 milligrams per square cm.

For comparison it may be mentioned that a hardened and tempered sample of nickel chrome steel containing three per cent. nickel and one per cent. chromium, which was tested along with the stainless samples, was badly corroded, the loss in weight being 3·6 milligrams per square cm.

On the other hand, the same stainless steel samples, after repolishing, were immersed for four days in a five per cent. solution of pure acetic acid, which has a much more powerful corroding action than vinegar (see page 184); in this

case the attack was greater with the samples tempered at higher temperatures, the losses in weight being :

Tempered 550° C....	3.1	milligrams	per square cm.
„ 600° C....	5.1	„	„
„ 700° C....	7.25	„	„

As a general rule it may be concluded that whatever differences exist between the resistances to corrosion of samples tempered at 600° and those tempered at higher temperatures, they are very slight and may be ignored, and that hence the actual tempering temperature, in the range 600° to 750° C., for any article of stainless material may be selected so as to produce the most desirable mechanical properties obtainable by tempering in this range of temperature.

Annealing. It has been shown that the microstructure obtained on annealing stainless material at a temperature above the carbon change point but insufficiently high to dissolve all the carbide, is granular, being very similar to that obtained from the same steel after being hardened and then tempered at 700° to 750° C., except that the carbide granules are much larger. In this condition, the material is much softer than when hardened and fully tempered and it is somewhat less resistant to corrosion than the latter form.

The non-corrosive properties of material annealed at a sufficiently high temperature to give a pearlitic structure are of comparatively little importance. The mechanical properties associated with such a structure being comparatively poor, it is hardly probable that material would be consciously put into service in such a condition. On general theoretical grounds it would be expected that a given steel would have less resistance to corrosion in such a condition than after any other form of heat treatment and experiments confirm this.

As illustrating the difference between annealed and hardened and tempered material, the following results of vinegar tests may be of interest. Steels of the following analysis :—

		Carbon %		Chromium %
<i>A</i>	...	0.31	...	11.1
<i>B</i>	...	0.32	...	12.2
<i>C</i>	...	0.33	...	13.3
<i>D</i>	...	0.31	...	14.4

were tested, after heat treatment in various ways, with vinegar, in the manner described on page 156. After hardening from 900° to 950° C., all four steels were quite stainless. When fully tempered at 750° C., *A* stained, *B* had a very slight stain but was in fact almost stainless, while *C* and *D* were quite unstained. After annealing at 900° C., *A*, *B* and *C* were stained by the vinegar while *D* was practically stainless. Similar results were obtained by annealing at $1,050^{\circ}$ C.

The etching effects of picric acid on samples for microscopical examination, which were noted in Chapter II (page 37) have also an interesting bearing on this point. In general, it is found that the ordinary alcoholic solution of this acid which is used for etching carbon steels, has no effect on a normal stainless steel when this is either hardened or hardened and tempered. The same steel in the annealed condition, however, may as a rule be etched by this solution, though somewhat slowly.

It may be concluded, therefore, that after annealing, stainless steel is less resistant to corrosion than after other forms of heat treatment. Even in this condition, however, it rusts extremely slowly. It is well to remember, in fact, that the differences produced in the resistance to corrosion of a sample of stainless steel by varying heat treatment are of considerably less magnitude than the difference between the resistance of such steel and that of ordinary carbon steel.

Cold Work. Although, possibly, not strictly a condition of heat treatment, it may be convenient to consider here the effects of cold work on the resistance of stainless material. Most metals, when distorted by cold work, have a greater tendency to corrode than they have in the normal condition. Stainless steel is no exception to this, and when severely distorted it rusts comparatively readily; for example, a coil of severely cold drawn wire will rust into a solid mass if left exposed to the atmosphere for a few months. The comparative resistance of distorted and undistorted material may be shown, for example, by placing half of a broken tensile test piece of hardened and tempered stainless steel (which had been polished all over before breaking) in a solution of common salt; corrosion will commence at the distorted end. The effects of cold work in accelerating corrosion are also shown rather strikingly in Fig. 76. The sample represented here, a piece of hardened and tempered

Plate XVII



FIG. 76. Effect of distortion on the rate of attack of dilute sulphuric acid on stainless steel.

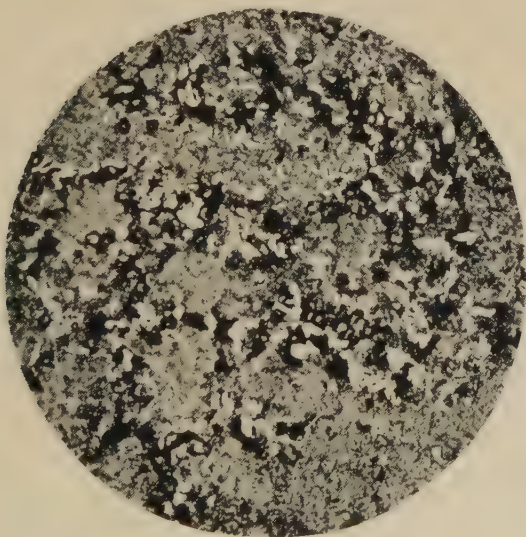


FIG. 77. Corrosion round particles of free carbide in high carbon stainless steel. $\times 500$. (see page 163).

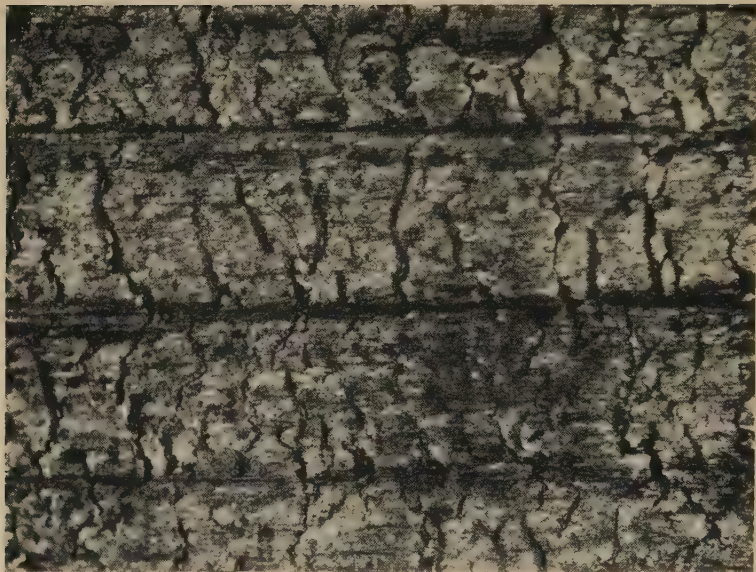


FIG. 78. Rough machined surface, showing cracks perpendicular to path of tool. $\times 12$.

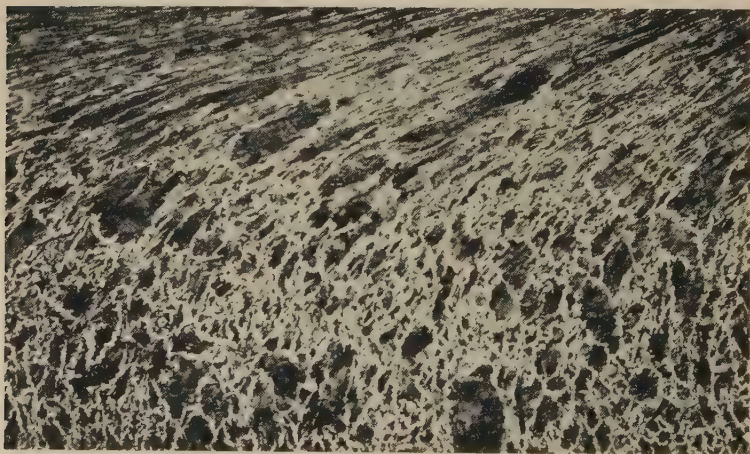


FIG. 79. Cross section through machined surface, showing distorted skin. $\times 100$.

stainless steel, had been cold stamped on one side with the figures 6 and 1. The stamp marks were afterwards just ground out, the surface polished on fine emery paper and the sample placed in five per cent. sulphuric acid for about eight hours. The distorted areas immediately under the original stamp marks had not been completely removed during the subsequent grinding and polishing operations and these were attacked more rapidly than the undistorted metal, with the result shown in the photograph.

Whether corrosion will or will not take place under stated conditions in a sample which has undergone a small amount of distortion, depends on the composition of the steel and can only be settled by actual experiment but the lessened resistance is always produced, just as it is by tempering a hardened sample. It is for this reason that a polished surface on stainless steel is more resistant than a roughly machined surface; the effect is due, however, not to the presence of polish on the former but to the absence of the distorted skin which is produced by the rough machining. There is also an indirect advantage in a polished surface; such a surface, being smooth, offers less opportunity for the lodgment of dust than a rough surface and, therefore, less chance of local pitting due to galvanic effects which are liable to be produced sometimes by dust.

In order to give some idea of the amount of distortion which may be produced by rough machining, Figs. 78 and 79 are of interest. The former shows the appearance of a planed surface of steel at a magnification of 12 diameters and one can see very distinctly the small cracks, perpendicular to the path of the tool, which are formed as the chips break off. It may be mentioned that the surface shown in Fig. 78 was not by any means very roughly machined, the actual feed of the tool being only $\frac{1}{16}$ inch wide.

The planings or turnings from such a surface are, of course, very badly distorted, but the surface which remains is also distorted for an appreciable thickness, as indicated in Fig. 79, which shows a section perpendicular to a machined surface. It will be seen that the surface is severely distorted in this case for a depth of about a hundredth of an inch. Such an effect is typical of what happens to a varying degree with all rough machining. In order that such a surface as that shown in Fig. 78 could be polished satisfactorily it

would have to be finely machined and ground, and both these operations produce surfaces which are very much less distorted than those produced by rough machining.

Effects Produced by Variations in Composition of Stainless Steel.

(1) **Carbon and Chromium.** These are the most important variables from the point of view of the corrosion of stainless steel. From the assumptions which have been made earlier as to the effect of free carbide and dissolved chromium on the resistance to corrosion of any given sample of stainless steel, it is obvious that the effects of variations in the content of either carbon or chromium must be considered in relation to the amount present of the other of these two elements.

Thus it will be evident that for any given chromium content, and with definite conditions of heat treatment, the resistance to corrosion will be greater, the lower the carbon content, while, on the other hand, with constant carbon, increasing the chromium will bring added resistance. From a commercial point of view, the mechanical properties required in the steel are in many cases equally as important as its degree of resistance to corrosion, and this aspect of the case frequently limits the allowable variations in composition to a considerable extent. For example, it has been shown earlier that with suitable treatment a steel containing only 8.6 per cent. chromium has notable non-staining properties. The mechanical properties of the sample after this necessary heat treatment, however, would be an effective bar to its use for many purposes. In a similar manner, raising the chromium content to 20 or 30 per cent. increases the resistance to general corrosion and minimises the effects of heterogeneity due, for example, to high carbon content; such alloys, unless of very high carbon content, as was indicated on pages 90 to 95, cannot be hardened to any extent by quenching and their mechanical properties are not suitable in many cases. For reasons such as these and from a purely commercial aspect, the cost of the higher chromium alloys being great, the amount of chromium usually found in stainless material lies between 11 and 14 per cent. Steels in this range containing less than about 0.40 per cent. carbon are stainless to vinegar when suitably hardened.

Steels are occasionally made, by accident or for special

purposes, containing more carbon than indicated above. Such steels may stain to some extent with vinegar when quenched from 900° to 950° C. On quenching from higher temperatures, however, they show an increased resistance to corrosion precisely in the same way as the lower chromium steel described earlier (page 156). There are, of course, limits to the amount of carbon which a steel containing 11 to 14 per cent. chromium could carry and still become stainless on quenching from high temperatures because, as was shown in Chapter II, the amount of carbon which can be dissolved by such steels under ordinary conditions of heating is not great, being in fact much less than in chromium-free steels. Thus a steel containing 1.0 per cent. carbon and 11.8 per cent. chromium still contained a considered amount of free carbide after being quenched from $1,100^{\circ}$ C. and under the vinegar test described earlier it stained. On the other hand, a steel containing 0.96 per cent. carbon and 13.1 per cent. chromium, which stained with the vinegar test after being quenched from 950° C., was quite unattacked by this test when quenched from $1,050^{\circ}$ C., although there was still a large amount of free carbide present. The difference between the behaviour of these two steels under the vinegar test is understandable from the difference in their chromium content.

An interesting example of the effect of the free carbide, existing in a high carbon stainless steel, in causing electrochemical corrosion is seen in Fig. 77. This represents part of the attacked surface of the sample containing 11.8 per cent. chromium, mentioned above, after it had been tested with vinegar; it is readily seen that the dark deeply corroded areas lie in close proximity to the large particles of free carbide which are visible in the section.

Owing to the very low carbon content of the mild stainless steels, or stainless iron, the greater part of the chromium in such steels is in solution in the iron even when they are in the fully tempered condition. The actual composition of the carbide in such steels is not known at present but, as previously mentioned, the ratio of chromium to carbon in the carbide is probably about 10 to 1; hence the presence of 0.1 per cent. carbon would lock up in carbide form only about one per cent. of chromium. As a consequence of this, such mild steels are stainless to vinegar

when fully tempered, even when they contain rather less chromium than is customary in stainless material, e.g., 10 to 11 per cent.

Stainless irons containing large amounts of chromium, e.g., 14 per cent. or above, are exceedingly resistant to corrosion after any form of heat treatment. It is obvious that the effects of tempering or annealing on low carbon material will be less than on higher carbon steels, because the former contains considerably less carbide and, hence, changes in the physical condition of this are less likely to affect the resistance to corrosion of the material. These high chromium irons may also be cold worked to a considerable extent without appreciably impairing their corrosion resisting properties.

(2) **Silicon.** The effect of the presence of appreciable quantities of this element in raising the temperature at which the Ac.1 change occurs and also that necessary to obtain complete solution of the carbide has already been referred to (see page 117). It follows from this that correspondingly higher hardening temperatures are required with high silicon steels in order to obtain similar results in corrosion resisting properties.

With regard to general corrosion, the presence of about one per cent. silicon appears to have little effect. For example, comparative tests were made on two steels having the following analysis:—

		A	B
Carbon	0.39 %	0.38 %
Silicon	0.11 %	1.26 %
Manganese	0.22 %	0.28 %
Chromium	13.6 %	13.8 %
Nickel	0.64 %	0.66 %

After being oil quenched from 900° C. sample A was hard (Brinell hardness number 495) and stainless to the vinegar test; sample B after the same treatment was much less hard (Brinell hardness number 286) and it stained slightly with vinegar. Raising the quenching temperature to 950° C. increased the Brinell hardness number of sample A to 555 and of B to 430; in this condition both were unattacked by vinegar. After hardening and tempering, both stained slightly, B less so than A; similar results were obtained after annealing.

Samples of the steels were hardened and then tempered at 700° C. and in this condition were exposed to tap water for eight months; they were then both perfectly free from any signs of corrosion. Further samples of both steels which had been annealed at 900° C. were also quite unattacked after a similar exposure.

Other samples of the two steels after hardening and tempering were exposed to various acids and their losses in weight determined. The results obtained are given below, the losses in weight being expressed as milligrams per square centimetre of surface per hour.

Acid.				Strength.	Steel A. (0·11 % Si.)	Steel B. (1·26 % Si.)
Sulphuric Acid	5%	0·71	0·28
"	"	35%	11·2	3·03
"	"	50 %	0·60	0·87
Nitric Acid	Normal	0·56	0·24
Hydrochloric Acid	" (10%)	0·25	0·265
Acetic Acid	5 %	0·061	0·063
Oxalic Acid	Normal	0·030	0·030
Citric Acid...	6 %	0·11	0·05

These results indicate that the presence of about one per cent. silicon reduces the rate of attack of dilute sulphuric and nitric acids on the steel but has practically no effect on the rate of attack of weak organic acids (except citric acid) or of dilute hydrochloric acid or more concentrated sulphuric acid. The previous results showed that the silicon steel was slightly more resistant to the vinegar test when both steels were hardened and tempered, but it required a higher quenching temperature to produce stainlessness, while as regards ordinary corrosion the silicon appeared to have no effect on the resistance of the steels to ordinary tap water. As a whole, therefore, it may be concluded that the presence of about one per cent. silicon has little effect on the resistance of the steel to corrosion beyond reducing the rate of attack of some mineral acids. As the mechanical tests given on page 118 indicate that such an amount of silicon reduces the toughness of the steel to a considerable extent, it would appear that the presence of such a content of silicon is to be avoided, especially in material for engineering purposes.

A similar opinion was given as a result of tests carried out at Woolwich Arsenal on steels containing high (about 1.4 per cent.) and low percentages of silicon and with carbon up to 0.43 per cent.* As a result of these tests it was stated "The anti-corrosive influence of silicon was difficult to estimate in the case of steels containing more than 12.5 per cent. of chromium. In certain acid etching reagents, for example, high silicon steels were undoubtedly the more resistant to attack, but in the weather and sea water trials their superiority over low silicon varieties was not evident and, in fact, appeared to exist only in the tempered specimens of the higher carbon varieties."

(3) **Nickel.** Most samples of stainless material contain small but varying amounts of nickel; hence it is important to know what effect, if any, the presence of this metal may have on the resistance of the steel to corrosion, particularly as, in certain cases as mentioned in an earlier chapter (see page 71), the effect of about one or one-and-a-half per cent. may be beneficial from a mechanical point of view.

Comparative tests were made on two steels containing

		A	B
Carbon	...	0.39 %	0.39 %
Silicon	...	0.08 %	0.12 %
Manganese	...	0.10 %	0.32 %
Chromium	...	10.0 %	10.5 %
Nickel	...	0.42 %	2.24 %

The content of nickel in sample B is considerably higher than that normally found in stainless material; hence a comparison of these two steels will indicate the maximum effect likely to be produced by such variations in nickel content as are ordinarily found in stainless steels. The chromium content of the two samples is lower than usual, but this is an advantage rather than otherwise, since it will tend to emphasise any influence which the nickel may have.

Polished samples of these two steels, both in the hardened condition and also after hardening and fully tempering were exposed to the action of water for four months and in both cases the steels behaved in a precisely similar manner.

* "Metallurgical Data on Stainless Steels." H. H. Abram. *Chem. & Met. Eng.*, Vol. XXX (1924), p. 430.

There was a slight local attack in all cases at the point of support, the amount of attack being greater with the tempered specimens than with those which were hard, but no difference was observable between the two steels. Apart from this local attack, the samples retained their polish after the test.

The high nickel steel was somewhat more resistant to vinegar than the other, but the difference was very slight.

Samples of both steels, after hardening and tempering, were exposed to the attack of various acids with the following results, the losses in weight being expressed in milligrams per square centimetre of surface per hour :—

Acid.	Strength.	Duration of Attack.	Loss in Weight.	
			Steel A. (0·42% Nickel)	Steel B. (2·24% Nickel)
Sulphuric	... 5 %	6 hours.	1·26	1·19
Hydrochloric	... Normal.	„	0·39	0·94
Nitric	... „	„	9·34	8·66
Acetic	... 5 %	5 days.	0·051	0·042
Citric	... 6 %	24 hours.	0·035	0·025

It will be seen that the presence of about two per cent. nickel slightly reduces the rate of attack with all the acids tried except hydrochloric ; with this acid there was a marked increase.

The results indicate that the presence of about two per cent. of nickel has possibly a very slight beneficial effect on the resistance of the steel to vinegar and to most acids. For general purposes, the effect of such an amount of nickel on corrosion may be ignored and its presence adjusted, if necessary, to suit physical requirements.

The austenitic steels produced by the addition of much larger amounts of nickel possess very valuable properties not only from a mechanical point of view but also as regards their resistance to corrosion. Such steels will be considered in Chapter VII.

(4) **Copper.** This metal is not a common constituent of stainless material ; claims have been made, however, notably by Saklatwalla,* that the addition of about 0·5 to 1·5 per cent. copper to stainless steel very considerably improves the resistance of such steel to acids, notably sulphuric and

* " Ferrous Alloys Resistant to Corrosion." *Iron Age*, April 24th, 1924.

hydrochloric. In experiments carried out to investigate these claims, samples of steels containing :—

		A	B
Carbon	0·16 %	0·22 %
Silicon	0·28 %	0·28 %
Manganese	0·17 %	0·17 %
Chromium	12·1 %	12·1 %
Nickel	0·44 %	0·47 %
Copper	0·08 %	1·20 %

were hardened from 950° C. and tempered at 700° C. and were then exposed to the action of various acids for suitable periods and their losses in weight determined. The results obtained are given below; the losses, as before, being expressed in milligrams per square centimetre of surface per hour :—

Acid.	Strength.	Duration of Attack.	Loss in Weight.	
			Steel A. (0·08 % Copper)	Steel B. (1·2 % Copper)
Sulphuric	... 5 %	7 hours.	2·21	1·05
„	... 35 %	6 „	26·5	4·5
„	... 50 %	6 „	0·88	0·64
Hydrochloric	... Normal. (10 %)	7 „	0·58	0·18
Nitric	... Normal.	6 „	0·71	0·76
Acetic	... 5 %	24 „	0·032	0·016

It will be seen that the copper has a noticeable effect with all the acids used except nitric. However, although the addition of copper certainly reduces the rate of attack with most of the acids, the steel containing copper can hardly be described as an “acid resisting” material.

(5) **Scale.** Although scale is not strictly a variable in composition, it may not be out of place to consider its effects here. Stainless material, after heating to high temperatures, whether followed or not by rolling or forging, is coated with a scale consisting of the oxides of iron and chromium. This scale is electronegative to the metal and, if it is not removed, will cause local corrosion to occur in its neighbourhood. Such scale must therefore be removed either by suitable machining or by pickling. Sand blasting does not appear to be so

effective ; although the greater part of the scale is removed by this treatment, producing a very pleasing surface, small particles of it are liable to be hammered into the surface by the sand and thus remain to act as potential centres of corrosion.

It is obvious also that finished surfaces of stainless material should be free from roaks, pits or cracks, or even stamp marks formed by pressing a lettering die into the surface of the hot steel, because such marks and defects will contain scale. Scale occurring in stamp marks may generally be removed by careful pickling ; it is preferable, however, to etch identification marks on finished surfaces rather than to stamp them.

It is also evident that no amount of pickling or machining will remove the particles of scale present in wild or unsound steel, as fresh particles are exposed with each new surface. It follows, therefore, that articles made from stainless steel which contains much slag or which was unsound in the ingot will never be so satisfactory as those manufactured from properly made steel ; for example, knives made from such unsound steel develop in use a mottled appearance due to the presence of minute pits formed from the slag or oxide inclusions present in the steel.

THE RESISTANCE OF STAINLESS STEELS TO
VARIOUS TYPES OF CORRODING MEDIA

CHAPTER VI

THE RESISTANCE OF STAINLESS STEELS TO VARIOUS TYPES OF CORRODING MEDIA

In the following pages an attempt has been made to indicate the resistance of stainless material to various types of corroding media, in the hope that the accounts given of the behaviour of the material under the conditions described may be of use in indicating in what directions stainless steels are likely to be useful as corrosion-resisting materials and also those in which they have no great value in this respect. The opinions expressed are based upon experimental work carried out in the laboratory over a period of some ten years, and also upon the results attending the use of the material for various engineering purposes. As it would be impossible to give any detailed account of the very large amount of experimental work which has been carried out, the author has contented himself with dealing in a more or less general manner with the subject. At the same time, the results of a number of experiments have been included in order to illustrate the opinions expressed; it may be mentioned, however, that these opinions are not founded solely on the results quoted, these being given merely as examples.

A considerable proportion of the laboratory work was undertaken to obtain data on specific problems. Owing to this, the experiments with some media have been carried out under conditions which are not strictly parallel with those used with other reagents, the conditions in each case being those best adapted to solve the particular problem in hand. Although this introduces a lack of uniformity of conditions which is perhaps not desirable in a series of scientific investigations, it does not introduce any serious difficulty in the practical application of the several series of results.

In discussing the corrosion of any metal or set of metals,

it is generally difficult to record adequately the comparative behaviour of the several samples. When the attack of any reagent is practically uniform over the whole surface of a sample of metal, the loss of weight of the sample (expressed in terms of surface area and time) is of some value in comparing the rate of attack of different samples, providing that all such samples are tested under identical conditions. Figures thus obtained, however, should only be used for comparison among themselves as they are liable to vary considerably should any of the conditions of the test be altered, such for example as duration of test, volume of fluid, movement of fluid, size and shape of the sample and, in rolled or forged material, its orientation with respect to the direction in which the metal has been elongated. Where, however, corrosion takes place by local attack, as is often the case, figures giving loss of weight are of little value in themselves and are only of use to the experimenter in helping him, when examining the corroded samples, to form an idea of the intensity of the local attack. No attempt has therefore been made, in the results which are quoted, to give detailed figures showing loss in weight where the attack has been local in character. When figures are given, it should be understood that they are only intended to be comparative among themselves and to indicate the intensity of the attack on the several samples under the conditions of the experiment. For this reason, comparable pieces of mild steel have generally been included in the tests. In all cases where no analysis or treatment is quoted, it is to be understood that the stainless material was of normal composition and had been hardened and then fully tempered, in the range 650° to 700° C., so as to give tough ductile material with a tensile strength of about 40 to 60 tons per square inch depending on the carbon content. Except when otherwise stated, all tests were carried out at atmospheric temperature; this applies also to the experiments mentioned in the previous chapter.

In recording the results of experiments in which the attack on the sample was uniform in character, the loss of weight is generally given in terms of milligrams per square centimetre of surface of the sample per hour. The milligram was chosen as the unit of weight in preference to the gram in order to avoid long strings of cyphers after

the decimal point. Such a measurement of the loss in weight in terms of surface area and time, while probably giving the most complete information, may not perhaps allow such an easy visualisation of the actual losses which the several samples have sustained and, for this reason, figures giving the loss in weight as a percentage of the original weight of the sample have in most cases been included as well.

Atmospheric Corrosion. The effect of this depends on the location of the test. In towns, and especially in the neighbourhood of works, the atmosphere contains distinct amounts of acid and large amounts of dust, often ferruginous in character. Samples exposed for prolonged periods to such atmospheric conditions become coated with a dark brown coating which is often so tenacious that it may only be washed off with some difficulty. When the coating is removed, the surface of the metal underneath is sometimes found to be almost unimpaired. At other times it is more or less covered with fine pits. The author has some samples which have been hung outside the window of his laboratory in the steel works at Attercliffe, Sheffield, for four years. They are covered with a thick brown coating of ferruginous dust. On scraping portions of this off, however, the original polished surface of the samples is seen to be still present to a great extent though marred, as a polished surface, by the presence of minute pits. The actual amount of corrosion, however, is exceedingly small and it appears to have come almost to a standstill; thus the pitting in the samples does not appear to have increased to any great extent during the last two years.

Although the pitting mentioned above detracts from the value of stainless steel where a permanent polished surface is essential even under the adverse conditions of town atmosphere, it should be noted that the conditions to which these samples were subjected were severe in the extreme; thus they were exposed continuously to the weather and were never wiped or cleaned at all. If the samples were cleaned periodically, the pitting would be much less noticeable.

Under less severe conditions, as for example, in the purer atmosphere of the country or indoors, even in town, stainless material will remain unattacked for long periods. The author has had three aeroplane valves made of stainless

steel in continuous use as paper weights on his desk at the works for over six years; they show practically no signs of attack at all.

There is also one aspect of the matter which has an important bearing on the use of stainless material for the manufacture of fittings exposed to the atmosphere. Although the pitting described above detracts to a considerable extent from the appearance of a polished surface, the actual loss by corrosion under such circumstances is exceedingly small. Where, therefore, the ability to withstand marked corrosion is required rather than the absolute permanence of a polished surface, the use of stainless steel may offer great advantages. This may possibly be well illustrated by referring to the use of this metal for hinges for doors. An ordinary iron or steel hinge, exposed to the atmosphere, rusts fairly rapidly and a typical steel hinge when hung outside the author's laboratory had rusted so much in the course of about a couple of months that the two halves could not be moved relative to each other at all; in other words its value as a hinge had completely gone. A hinge of similar shape but made of stainless iron, hung beside it is still perfectly satisfactory as a hinge after an exposure of over three years. It is certainly coated with a brown film, and scraping a little of this away reveals minute pits in the surface of the steel, but neither the film nor the pitting affect the movement of the two parts to the slightest degree, and, as a hinge, it is still quite as serviceable as on the day it was made.

Tap Water is without action on stainless material in either the hardened or tempered conditions. The author has a number of small samples, turned from a bar of hardened and fully tempered steel, over which tap-water was allowed to trickle for two years, and they do not show the slightest signs of attack. These samples were contained in a wide glass tube which was attached to a water-tap; the latter, being open slightly, allowed water to trickle continuously over the samples.

Other samples have been immersed in slowly running water for months without showing the least signs of attack.*

* In the running water tests mentioned above, and also in the previous chapter, the samples were supported in a large glass bowl. A very slow stream of tap-water was led by a glass tube to the bottom of the bowl and allowed to overflow from the latter into the sink. By this means the bowl was kept constantly full of water and any fine dust which might have been deposited from the atmosphere of the laboratory was automatically carried away.

River and Well Water have, as a general rule, no appreciable action on stainless material. This is shown by the large number of pump rods and other fittings which are in use successfully in many parts of the country for pumping such water.

Sea Water and Brine have no general action on stainless material when the latter is completely immersed or alternately wet and dry. Thus samples of stainless steel and iron in the hardened and tempered condition were partly embedded in a block of wood and the latter then fixed to a jetty, on the sea coast, at a point between high and low water marks. The samples were thus alternately wet and dry. After six months' exposure they were quite bright and practically unattacked, only a few minute pits being formed; thus a sample weighing 150 grams and having a surface area of about 47 square centimetres had a total loss in weight, after the six months' exposure, of one centigram.

Under the prolonged action of a spray of sea-water, stainless steel is liable to be attacked, pitting being then generally produced.

The effect of any imperfections in the stainless steel itself are emphasized considerably more if it is exposed to sea-water than to tap-water. Thus the presence of surface defects containing scale, or of slag inclusions, or of local distortions are shown up more quickly under the attack of sea-water than of ordinary tap-water. Under such conditions, the attack generally takes the form of pitting and sometimes the pits reach a considerable depth.

If a sample of stainless steel is partly immersed for a long period in sea-water in such a way that the position of the level of the water on the sample is sensibly constant, the tendency to corrosion at this water line or very slightly above it is considerably greater than if the sample were completely immersed. Under such conditions of partial immersion, pitting is likely to be produced at the water level and slightly above it.

Ammonia, Alkalies and Alkaline Carbonates in all strengths of solution appear to have no effect on stainless material. Samples of the steel have also been placed for months in very damp atmospheres charged with ammonia gas without undergoing any attack.

Aqueous Solutions of Salts. It may be doubted whether the results of laboratory experiments in which samples of stainless steel (or any other metal) are placed or suspended in beakers containing various solutions are of any great practical value except in so far as they indicate whether attack does or does not take place and if it does, whether immediately or slowly. The results obtained simply refer to the conditions under which the tests were carried out and will vary as these conditions vary, so much so that the relative rates of corrosion of a number of samples which were more or less attacked by a given solution might alter to a considerable extent if changes were made in the conditions of the test, such as, for example, duration, depth under surface of liquid, method of support, or temperature.

When corrosion takes place in stainless steel under such conditions of test, it almost invariably starts at the point of support and often is entirely confined to that point. In such cases, therefore, the amount of corrosion or even the presence or absence of corrosion, will depend on how a sample is supported and conditions in which it rests against the bottom and sides of a glass beaker, or on a layer of paraffin wax, or is supported by a glass hook or is suspended by a piece of cotton are not likely to occur in the practical application of stainless materials! It is not intended therefore to give details of how particular stainless samples behaved when immersed in aqueous solutions of various salts. Speaking generally, it may be said that many such solutions have little or no effect on stainless material and when corrosion does take place it proceeds very much slower than with ordinary steel.

Solutions of the following salts, among others, appear to have no direct action on stainless steel. Corrosion of the sample at the point of support, when this is below the level of the liquid, is apt to take place with solutions of the salts marked with an asterisk; such solutions also appear to intensify the effect of local defects in the steel in the same manner as sea-water. In most cases the salts were tested in the form of 5 % solutions, the samples being immersed in the liquids for four to five weeks.

Alkaline Bicarbonates.

„ Carbonates

Alkaline Nitrates.

„ Sulphites.

Ammonium Oxalate.	Lead Acetate.
„ Persulphate.	*Magnesium Chloride.
„ Phosphate.	* „ Sulphate.
Copper Acetate.	Manganese Sulphate.
„ Nitrate.	Potassium Bichromate.
„ Sulphate.	„ Chlorate.
Ferric Nitrate.	* „ Chloride.
„ Sulphate.	„ Cyanide.
Ferrous Sulphate.	*Sodium Chloride.

On the other hand the following salts attack the steel to some extent and as the effects produced are sometimes of interest, they may be briefly mentioned.

Ammonium Chloride solutions are well known as corroding agents. They have a staining and pitting action on stainless material the extent of which, however, depends on the concentration of the solution. With dilute solutions, e.g., containing about five grams of the salt per litre, the attack is very slow even when the solution is hot. For example a small cylinder of stainless steel was kept totally immersed for ten days in such a solution at a temperature of 80° to 90° C.; at the end of that period the sample was stained a greyish tint and was slightly pitted in two places, the total loss in weight being under 0.06 grams. For comparison, a piece of mild steel similarly treated was badly corroded and lost ten times as much weight.

With regard to stronger solutions, a cylinder of stainless steel was immersed in a 25 % solution (at atmospheric temperature) for a month. There was then a slight general darkening of the polished sample and local attacks at the point of support and in a small area near the middle of the piece. The sample weighed 31 grams and had a total surface area of 17 sq. cm.; the total loss of weight during the month's immersion was only two milligrams.

Ammonium Sulphate solutions have little or no action when dilute but have a slow general attack when more concentrated. Thus cylinders of stainless steel were immersed in 5 % and 25 % solutions of the salt for 14 days. At the end of that period the sample in the more dilute solution was quite unattacked; that immersed in the 25 % solution had darkened and had a slight etched appearance. The total loss in weight, however, was only 0.01 per cent.;

expressed in terms of surface and time, this was equivalent to a loss of 0.013 milligrams per sq. centimetre per day. Samples of ordinary mild steel (of the same size and shape) lost, under the same conditions of attack, 0.12 per cent. in the 5 % solution and 0.082 per cent. in the 25 % solution.

With regard to hot solutions, the samples mentioned above were afterwards kept for 48 hours in solutions of the salt maintained at 80° to 85°C. The stainless steel in the 5 % solution remained quite unattacked after this test; that in the 25% solution suffered no further appreciable attack. The samples of mild steel similarly treated lost 0.16 % and 0.18 % of their weight, in the 5 % and 25 % solutions respectively, during the 48 hours' test.

Alum. Dilute solutions of either potash or ammonia alum have no action on stainless steel, thus samples of the latter were immersed in 0.2 % and 1.0 % solutions for 15 days without the slightest action taking place. With stronger solutions, however, there is a slow but distinct action. Thus samples of the steel were immersed for eight days in solutions of potash alum of the following strengths with the results indicated below. For comparison, results obtained from ordinary mild steel under similar conditions, are included.

Strength of Solution.	Loss in mgm. per sq. cm. per hour.		Per cent. loss.	
	Stainless Steel.	Mild Steel.	Stainless Steel.	Mild Steel
5 % 	0.012	0.065	0.125	0.69
Saturated (About 15%) ...	0.008	0.035	0.085	0.37

Ammonia alum gave similar results.

Ferric Chloride solutions, even when fairly dilute, attack the steel. A sample of stainless steel, immersed for 24 hours in a solution containing 8 grams of ferric chloride per litre, was attacked at the rate of 0.27 milligrams per square centimetre of surface per hour, the total loss of weight during the period amounting to 0.41 per cent. of the weight of the sample. After the attack, the appearance of the sample was similar to that produced by deep etching with acids.

On the other hand, samples of stainless steel were immersed in 5 per cent. solutions of *ferric sulphate*, *ferric nitrate* and *ferrous sulphate* for five weeks, in each case without being attacked in the least. Concentrated solutions of ferric sulphate and nitrate have also no action on the steel. In addition to this, ferric sulphate, when present in sufficient amount, has the property of preventing the attack of sulphuric acid on stainless steel while ferric nitrate has a similar effect with nitric acid. These effects will be considered in some detail later (see pp. 193 & 206). Curiously enough ferrous sulphate does not appear to act in the same way as ferric sulphate in preventing the action of sulphuric acid.

Copper Chloride solutions also attack stainless steel. With strong solutions, a deposit of copper is formed on the steel, the latter being dissolved quite rapidly. With dilute solutions on the other hand, pitting takes place and very little copper is deposited. Thus small samples of stainless steel exposed for 24 hours to the following solutions were attacked as indicated below :—

Strength of Solution.	Per cent. loss in wt. of sample.	Character of Attack.
0.1 %	0.02	One deep pit, otherwise unattacked.
1.0 %	0.77	Pitting and local corrosion.
10.0 %	28.0	General attack, sample covered with thick deposit of copper.

On the other hand, solutions of *copper sulphate*, *copper nitrate* and *copper acetate* have no action on stainless steel. For example, a sample was placed in a three per cent. solution of copper sulphate and the latter boiled to dryness, occupying two hours and a half in the process; there was not the slightest sign of attack.

In addition to having no action itself on stainless steel, copper sulphate also, under certain conditions, greatly retards and in some cases altogether prevents the action of sulphuric acid on the steel. Copper nitrate also acts similarly with dilute nitric acid. These effects will be con-

sidered later in connection with the attack of these acids on stainless material (see pp. 187 and 206). Copper acetate also has a similar action with acetic acid; thus a sample of stainless steel was immersed for twenty-four hours in a ten per cent. solution of this salt in water containing three per cent. of acetic acid and was unattacked although acetic acid of this strength has a slow action on the steel.

Mercuric Chloride solutions attack stainless steel very rapidly; a sample immersed in a five per cent. solution of this salt lost 1.64 per cent. of its weight in twenty-four hours.

Sodium Sulphate solutions, when dilute, e.g., about five per cent., have no action on stainless steel though corrosion is apt to take place at the point of support of a sample when it is immersed in such solutions. Concentrated solutions, however, have a slow general action on the steel. Thus a sample immersed for twenty-eight days in a saturated solution of the salt lost 0.16 per cent. of its weight, or at the rate of 0.0043 milligrams per square centimetre of surface per hour. It may be noted that such a concentrated solution has a strongly acid reaction to litmus.

Solutions of *potassium sulphate* behave in a similar manner to those containing sodium sulphate.

Vinegar and Fruit Juices. The use of stainless steel for cutlery purposes has been the cause of the very general use of vinegar as a kind of test reagent for stainless material and its effects, or lack of them, have been referred to several times in the preceding pages.

Commercial vinegars vary to some extent in their corrosive action. The tests which are quoted in this book were obtained by the use of pure malt vinegar, of good commercial quality, containing four to five per cent. of acetic acid. Some commercial products, however, contain distinct amounts of sulphuric acid; such "vinegars" have a distinctly greater action on stainless material than the pure article.

The vinegar test with stainless steel is most usually carried out by placing a drop of the vinegar on a polished surface of the steel to be tested and allowing the drop to dry naturally; generally the sample is left over-night undisturbed. After the dried remains of the vinegar have been removed by washing, the surface of the steel is examined

Plate XIX

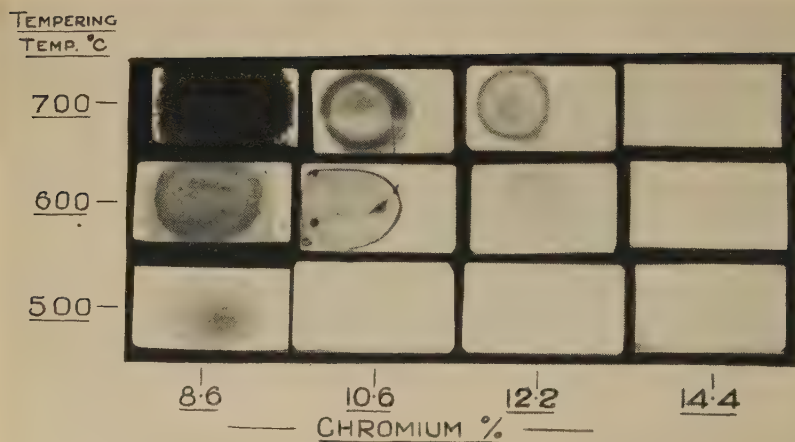


FIG. 80. Effect of chromium content on the resistance to staining, by vinegar, of stainless steels of cutlery temper, after hardening and then tempering as indicated.

To face page 188.]

for any signs of a stain; such a stain, when produced, generally takes the form of a grey mark on the polished surface, the vinegar having then an etching action. The "spot" test described above is a more severe test than that obtained by immersing the sample in vinegar for twelve or twenty-four hours.

Stainless steel containing about nine per cent. of chromium and upwards and with the ordinary carbon content for cutlery, i.e., about 0.3 to 0.4 per cent., when suitably hardened is entirely unaffected by the vinegar spot test.

The hardening temperature required to produce stainlessness will be in the neighbourhood of $1,000^{\circ}\text{C}$. when the chromium content is about nine per cent. but falls as the percentage of chromium rises. Similarly, lowering the carbon content reduces the hardening temperature required to produce stainlessness. On tempering such hardened material, no appreciable effect on the resistance to the vinegar test is produced up to a temperature of about 500°C .; after tempering at still higher temperatures, however, it may or may not stain depending on composition. With sufficient chromium it will remain stainless to the vinegar test after tempering at any temperature, but with less chromium than this, staining is produced after tempering at some temperature which is lower, the lower the chromium content. The amount of chromium required to produce complete resistance to vinegar is higher the more carbon the steel contains but with cutlery steel containing carbon as noted above, about 13 per cent. chromium is required. With low carbon irons, the material remains stainless to vinegar after being fully tempered when the chromium content is considerably lower than this.

The effect of varying chromium content on the resistance to staining of steels of cutlery temper is illustrated in Fig. 80, in which are shown the results of testing specimens of such material after suitable hardening followed by tempering at the temperatures indicated.

When the steel is in the annealed condition a still greater amount of chromium is required (for any given carbon content) in order to induce stainlessness; an example of this was given on page 159.

Although fully tempered samples of steel containing

less than about 13 per cent. of chromium may stain when spot-tested with vinegar, the attack of this reagent on such soft material is really extremely slow.

The use of vinegar as a test reagent for steel for cutlery purposes and for finished stainless cutlery is justified from the fact that vinegar is probably one of the most corrosive materials which such cutlery will have to resist in its ordinary use. The use of vinegar as a test for material for purposes other than cutlery, however, has not the same justification and although it has advantages in indicating in a general way the combined effect of varying composition and heat treatment, its indications do not determine whether or not a given sample will corrode when exposed to other media, e.g., ordinary tap water. For example a drastically annealed sample of steel containing 0.32 per cent. carbon and 12.2 per cent. chromium, which stained badly when tested with vinegar in the manner described above, was immersed in tap-water for ten months without showing the least sign of attack.

Fruit juices in general have an effect on stainless steel similar to that of vinegar, although the degree of their corrosive power probably varies to some extent.

It is interesting to note that the acids found in vinegar and fruit juices, when used in the form of pure solutions, have sometimes a distinctly greater effect on stainless steel than the corresponding natural juices. Thus, as will be seen later, a solution of pure acetic acid in water, of the same strength as that in vinegar, has a much greater effect than the latter on the steel; similarly, although lemon juice does not attack stainless steel, a solution of pure citric acid of the same strength exerts a distinct though slow corrosive action.

The reason for the difference between the effects of vinegar or natural juices as compared with the pure acids contained in them lies, in all probability, in the fact that the natural products contain organic compounds in colloidal solution. Such colloidal solutions have been found to exert a retarding action on the attack of other metals under diverse conditions: for example, very dilute solutions of starch or of egg albumen, in both of which the organic matter is in a colloidal state, corrode ordinary steel much more slowly than does water free from these colloids. This retarding action increases with the amount of colloid present

and, as Dr. Friend has pointed out,* it has a very considerable practical importance; thus most culinary operations deal with substances more or less colloidal in character and these, by passing into the water used in such operations, retard considerably the corrosion of the cooking utensils. The noteworthy point, however, in connection with stainless material is not so much the fact that retardation of corrosion occurs, but that this retardation is sufficient to prevent entirely the action of the natural juices on the stainless material when the latter has been suitably heat treated.

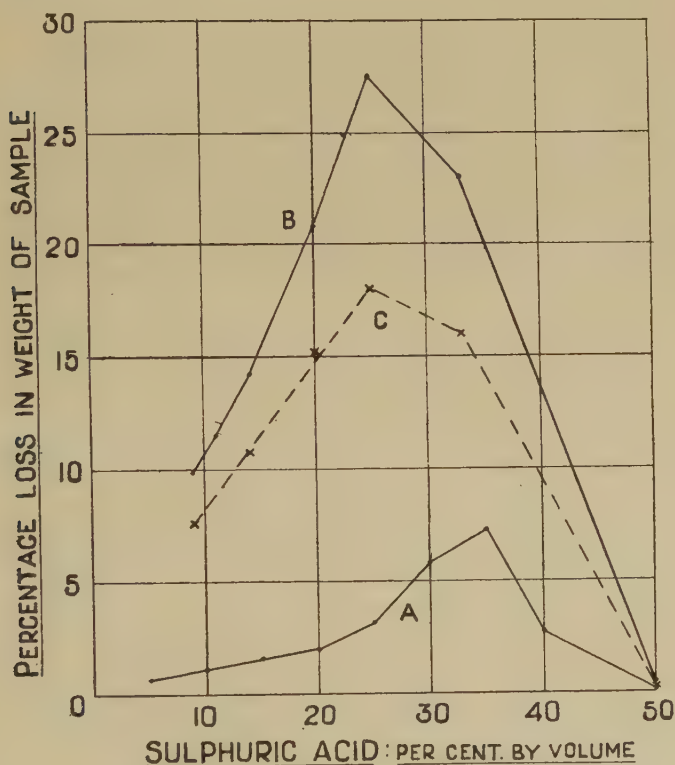


FIG. 81. Percentage loss in weight of stainless steel and mild steel after attack by sulphuric acid of various strengths.

- Curve A. Stainless steel, four hours' attack at atmospheric temperature.
 " B. Stainless steel, fifteen minutes' attack at 90°/95°C.
 " C. Mild steel, fifteen minutes' attack at 90°/95°C.

* "The Corrosion of Iron," J. N. Friend. Carnegie Schol. Mem. (Iron and Steel Inst.), 1922. p. 144.

Sulphuric Acid attacks stainless steel or iron rapidly. The action of this acid on high chromium steels has been known for a considerable time ; the following notes, however, will serve to indicate how the rate of attack is affected by varying composition of the steel and by the strength of the acid.

The effect of varying strength of acid is shown by the curves A and B in Fig 81, which give the percentage losses in weight of samples of hardened and tempered stainless steel, containing 0.25 per cent. carbon and 12.1 per cent. chromium after attack by sulphuric acid of different strengths at ordinary temperatures, and at 90° to 95° C. respectively. The duration of attack was four hours in the former case and fifteen minutes in the latter. The strength of acid is given as a percentage by volume. The results indicate that the maximum rate of attack, for short periods at atmospheric temperature, is produced with acid of about 35 per cent. strength while at higher temperatures a somewhat more dilute acid has the quickest action. Curve C gives for comparison the results obtained from a mild carbon steel (0.35 % carbon ; 0.23 % silicon ; 0.71 % manganese) when attacked under the same conditions as the stainless steel in curve B. The two steels apparently behave in a similar manner but the stainless steel is attacked rather more rapidly than the mild steel. With both steels, the rate of attack decreases very rapidly when the strength of the acid exceeds about 35 to 40 per cent.

Comparative figures for attack at atmospheric temperature of 5 %, 35 % and 50 % acid on stainless steel (hardened and tempered) and mild steel are given below.

Strength of Acid.	Duration of Attack.	Loss in mgm. per sq. cm. per hour.	
		Stainless Steel.	Mild Steel.
5 %	6 hours.	1.98	3.16
35 %	6 hours.	15.8	11.55
50 %	6 hours.	0.50	0.23
50 %	24 hours.	0.26	0.10

With the 50 per cent. acid, the rate of attack on both steels fell off rapidly after the first three or four hours; this is shown by the diminished rate of attack during the 24-hour period as compared with the shorter attack of six hours. No such falling off in the rate of attack is noticeable with the more dilute acids.

It was mentioned earlier (page 181) that both copper sulphate and ferric sulphate, under certain circumstances, prevent the attack of sulphuric acid on stainless material. In addition to being of distinct interest from a scientific point of view, the effect of these salts on the action of sulphuric acid has considerable practical importance. Many mine waters, which are notoriously corrosive in their action on pumping machinery owing to the presence of free sulphuric acid, contain also appreciable quantities of either or both of these salts, and as a result they have often no effect on stainless steel though they attack ordinary steel and other metals quite rapidly. It is not out of place, therefore, to devote some attention to the action of these salts.

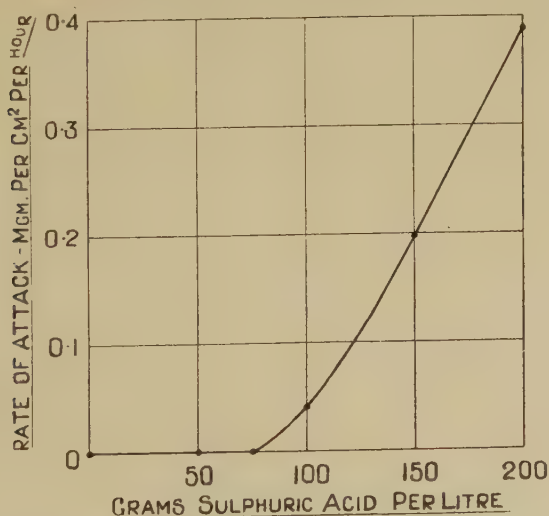


FIG. 82. Rate of attack (on stainless steel) of solutions of copper sulphate, 100 grams per litre, containing also the amounts of free sulphuric acid indicated.

The effect, on stainless material, of solutions containing both copper sulphate and sulphuric acid depends on the actual and the relative amounts of these two substances present.

in solution. A solution of copper sulphate itself, as mentioned earlier, has no action on stainless steel ; on gradually adding sulphuric acid to the copper sulphate solution, no action takes place until a certain amount of acid is present, the amount depending on the chromium content of the steel and on the actual concentration of the copper sulphate in solution. After this critical amount is exceeded, the action of the acid liquor becomes more and more intense as the concentration of acid increases. This is illustrated by the curve in Fig. 82, which gives the results of the action for twenty-four hours at atmospheric temperature of solutions, each containing 100 grams of copper sulphate* per litre but with different amounts of sulphuric acid, on a number of hardened and tempered samples of stainless steel containing 0.30 per cent. carbon and 12.6 per cent. chromium. Attack was produced when the concentration of free acid reached 100 grams per litre.

On adding copper sulphate in small but gradually increasing amounts to sulphuric acid, the action of the latter on stainless steel at first increases rapidly. In such cases, copper is deposited as a flocculent mass on the steel and no doubt sets up electrochemical action. As the concentration of the copper increases, however, the attack suddenly falls off very rapidly and finally, with the presence of sufficient copper sulphate, ceases altogether. These effects are shown in curves A and B in Fig. 83. The former refers to the attack of liquor containing 100 grams sulphuric acid per litre and the latter to solutions containing 50 grams of the acid per litre. The duration of attack in all cases was 24 hours at atmospheric temperature and the stainless steel was similar to that used for the previous experiment. The curves show that the amount of copper sulphate required to prevent action varies with the acid strength and is relatively less as the concentration of acid is lowered.

The resistance of stainless steel to the attack of the sulphuric acid when sufficient copper sulphate is present would appear to be due to a species of passivity somewhat similar to that produced in ordinary steel by strong nitric acid and other re-agents, as mentioned on page 153. There are also other points of resemblance, thus the passivity

* In all the results with this salt, the weights given refer to the crystalline material ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$).

produced in stainless steel by the action of copper sulphate persists for some time after the sample is removed from the solution producing passivity. This is notably the case if the samples are transferred to solutions in which the concentration of copper sulphate is gradually reduced. For example,

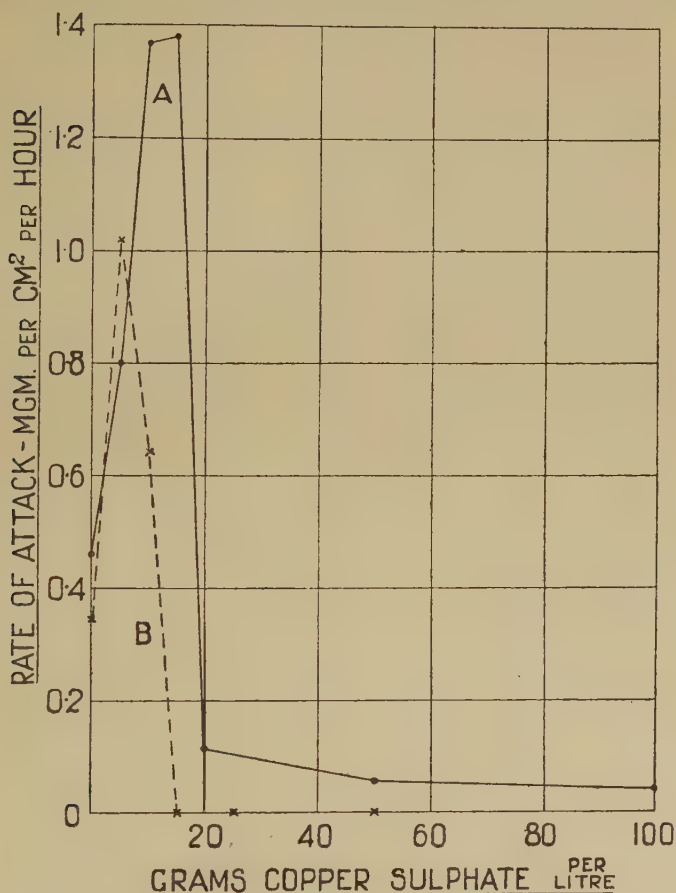


FIG. 83. Effect of copper sulphate on the rate of attack of dilute sulphuric acid on stainless steel.

Curve A. 100 grams free sulphuric acid per litre.

„ B. 50 „ „ „ „ „ „ „

a sample of stainless steel was placed in a solution containing 50 grams each of sulphuric acid and copper sulphate per litre; such a solution, as shown in Fig. 83, has no action on the steel. At intervals of one or two days, the sample was

transferred to solutions containing the same amount of free acid but with gradually decreasing amounts of copper sulphate. The concentration of the latter was reduced to 2.5 grams per litre without any action taking place, although under normal conditions the steel was attacked by similar acid liquor containing 10.0 grams or less of copper sulphate per litre. On reducing the strength to 2.0 grams per litre, the steel was very slowly attacked, the attack consisting of a gradual darkening of the surface. The sample was allowed to remain in this acid liquor for seven weeks; at the end of this period, the sample had a polished black surface, with a greenish tint, very similar to that of the "oxidised" finish of ordinary steel. The total loss in weight of the sample in the seven weeks' attack was only 0.014 per cent. of its original weight, equivalent to a rate of attack of 0.00024 milligrams per square centimetre per hour.

In the same way the concentration of copper sulphate in acid liquor containing 100 grams sulphuric acid per litre, in which a similar piece of stainless steel was placed, was gradually reduced from 250 grams to 7.5 grams per litre without any action taking place. When reduced to five grams per litre, however, a similar slow action to that described above took place; the sample gradually acquired a polished black surface and after seven weeks' attack had lost 0.019 per cent. of its original weight, equivalent to a rate of attack of 0.0003 milligrams per square centimetre per hour.

The extent of the passivity produced in these two cases will be more easily realised when it is remembered that under normal conditions, the samples would have lost well over 50 per cent. of their weight during a seven weeks' immersion in such acid liquors.

The passivity produced by acid copper sulphate solutions of suitable strength also persists for some considerable time if the samples are taken out of the solution producing passivity, dried and then left in this condition. For example, the sample used for the test in liquor containing 50 grams of sulphuric acid and 25 grams of copper sulphate per litre (Fig. 83, curve B) was cleaned and dried after the 24 hours' immersion, which produced no attack, and put away in a box for two months. It was then placed in liquor containing 100 grams of acid and 10 grams of copper sulphate, i.e.,

liquor which, as shown in curve A, Fig. 83, attacks the normal material rapidly. No action was visible for three or four days, after that the sample gradually darkened in colour. At the end of 34 days it was taken out and had a shiny greenish black surface similar to the two samples described above. The total loss in weight produced in the 34 days' attack was 0.009 per cent. of the original weight, equivalent to 0.00019 milligrams per centimetre per hour.

Again the passivity effect is rendered more striking by noting that a similar sample which had not previously been made passive lost practically 1.9 per cent. of its weight in 24 hours when immersed in acid liquor of this same strength and would therefore have lost considerably more than half its weight in 34 days.

The effect of copper sulphate was first noticed in the course of an investigation on the properties of a series of low carbon steels with gradually increasing chromium content; as the results then obtained show the effect of varying chromium content on the passivity produced with copper sulphate solutions, they may be quoted. The series of steels had the following analysis :—

Mark	Carbon %	Silicon %	Manganese %	Chromium %
A.	0.16	0.12	0.73	nil.
B.	0.14	0.14	0.12	4.72
C.	0.12	0.24	0.28	6.2
D.	0.09	0.17	0.11	7.5
E.	0.18	0.15	0.14	8.8
F.	0.16	0.17	0.12	10.0
G.	0.15	0.86	0.29	10.9
H.	0.09	0.77	0.24	12.0
J.	0.14	0.64	0.21	13.1
K.	0.09	0.30	0.17	14.0
L.	0.10	1.10	0.17	15.5
M.	0.13	0.90	0.27	17.5

Samples of each steel, in the form of discs one inch diameter and 0.25 inches in thickness were placed for 20 hours in a solution containing five per cent. of copper sulphate. Samples A, B and C were strongly attacked. The rest were unattacked. Samples D to M were then put back

in five per cent. copper sulphate containing one per cent. of free sulphuric acid ; sample D was immediately attacked and E more slowly. At the end of five hours these two had lost 0.6267 and 0.1040 grams respectively. F was very slowly attacked by the same solution, losing only 0.0683 grams in 27 hours. The other samples, G to M, were unattacked ; they were then transferred to solutions in which the amount of acid was gradually increased. With five per cent. free acid, G resisted the attack for six or eight hours, but afterwards was strongly attacked. The rest were quite unaffected after being in this or in 10 per cent. acid for three days. They were then transferred for two days to solutions containing 15 per cent. acid and then for five days to solutions with 20 per cent. acid. Sample H then showed a very slight etching effect but had no weighable loss ; the others were quite unattacked. All the samples were then placed for three days in liquor containing 25 per cent. acid. The surface of H was then slightly darkened, but again there was no weighable loss. The others were unaffected.

In all the solutions up to now, the concentration of copper sulphate had remained constant at five per cent., the amount of acid being gradually increased. In the succeeding tests, the acid content was kept constant at 25 per cent. and the concentration of copper sulphate gradually reduced. The results obtained are set out below :—

Strength of Liquor.		Length of Attack.	Sample.				
Sulphuric Acid.	Copper Sulphate.		H.	J.	K.	L.	M.
25 %	4 %	4 days	Darkened slightly more.	No attack	No attack	No attack	No attack
"	3 %	2 days	No perceptible change.	"	"	"	"
"	2 %	24 hrs.	Attacked	"	"	"	"
"	1 %	"	—	"	"	"	"
"	0.5 %	4 days	—	Attacked	"	"	"
"	0.25 %	35 "	—	—	Attacked	"	"
"	0.125 %	8 "	—	—	—	"	"
"	0.062 %	16 "	—	—	—	"	"
"	0.04 %	12 "	—	—	—	"	"
"	0.02 %	8 "	—	—	—	"	"
"	0.01 %	2 "	—	—	—	"	"
"	nil.	3 "	—	—	—	"	"

Samples L and M were subsequently transferred to a solution of sulphuric acid, copper free, in which the amount of acid was gradually reduced to 20 per cent., 15 per cent., 10 per cent., 8 per cent., 7 per cent., 6 per cent., 5 per cent., 4 per cent. and 2 per cent., the total time in these solutions being 14 weeks. At the end of that time, these two samples still remained perfectly bright and unattacked.

Besides indicating briefly the effect of increasing chromium content on the passivity produced by copper sulphate solutions, this experiment also shows the remarkable amount of passivity which may be produced when the chromium reaches 15 per cent. or over, especially when it is remembered that such high chromium irons are normally very strongly attacked by sulphuric acid. It may also be noted that samples H, J and K resisted for six or eight hours the solutions which finally attacked them; in each case, however, the attack was very prominent in less than 24 hours.

The action of ferric sulphate in retarding or preventing the attack of sulphuric acid on stainless steel was first pointed out by Dr. Hatfield and his results (quoted in the booklet, "The Development of Stainless Steel," published by Messrs. T. Firth & Sons, Ltd.) indicate that the amount of ferric sulphate required to prevent action varies with the condition of the steel, whether hardened or hardened and tempered, and also, with any one material, is proportional to the amount of free sulphuric acid present. In the case of hardened and tempered material, no attack was found if the concentration of the ferric sulphate was twice that of the free sulphuric acid while with hardened material the same effect was produced when the amount of ferric sulphate present was equal to one-fifth that of the free sulphuric acid.

Experiments carried out by the author on hardened and tempered material containing 0.3 per cent. carbon and 12.6 per cent. chromium are given in Table 22, and indicate that passivity with such material is produced with a less amount of ferric sulphate than Dr. Hatfield's experiments indicated. The concentration of the solutions are given in grams per litre.

The actual concentration of ferric sulphate producing passivity is probably affected to some extent by variations in temperature, or other conditions. Thus a duplicate

sample in liquor containing 15 grams ferric sulphate per litre, tested a few days after the one described in Table XXII, remained quite unattacked after being immersed for a month in the liquor.

TABLE XXII

Action of Ferric Sulphate on the attack of Sulphuric Acid on Stainless Steel.

Strength of Solution. (grams per litre)		Duration of Test.	Loss %	Loss in mgm. per sq. cm. per hour.
Sulphuric Acid.	Ferric Sulphate.			
100	nil.	24 hours.	0.76	0.56
"	5	"	0.86	0.62
"	10	"	0.94	0.66
"	15	"	1.0	0.73
"	20	36 days.	Not attacked.	—
"	40	"	"	—
"	60	"	"	—

It will be seen that there is a slight increase in the rate of attack when only small amounts of ferric sulphate are present, though the increase is not nearly so great as with copper sulphate and understandably so. As with the latter salt also, the passivity produced by ferric sulphate persists for some time after removing from the solution producing passivity but apparently to a less degree than with the copper salt. For example, a sample of material similar to that used for the tests above was placed for 24 hours in liquor containing 100 grams each ferric sulphate and sulphuric acid, there being of course no attack. It was then transferred to solutions containing the same amount of acid but with the ferric sulphate reduced successively to 50, 25, 15, 10, 5 and 2.5 grams per litre; in each case there was no attack. The sample was left in each solution for 24 hours. The sample was then transferred to a similar solution but containing only 2.0 grs. ferric sulphate per litre and was vigorously attacked in a few minutes, the rate of attack being similar to that of such liquor on the normal steel.

It has been mentioned that ferrous sulphate has not the same effect as ferric sulphate; thus a sample of stainless

steel placed for 24 hours in a solution containing 100 grams sulphuric acid per litre together with 200 grams ferrous sulphate per litre was attacked at practically the same rate as a similar sample placed in acid of the same strength but containing no ferrous sulphate, the rates of attack being 0.39 and 0.46 milligrams per square centimetre per hour respectively.

The practical importance of these interesting passivity effects lies, as mentioned earlier, in their application with regard to the pumping and handling of acid mine waters and other water containing free sulphuric acid. Providing a sufficient amount of either ferric sulphate or copper sulphate or both is present in the water along with the free acid (and often mine waters contain these salts in relatively large quantities) such water will have no action on stainless steel though it will attack ordinary steel quite rapidly. Two cases of such mine waters, which the author had recently to investigate, may be instanced. These waters had the following analyses, expressed in parts per 100,000.

	A.	B.
Copper	16	14.7
Ferric Iron	188	71.2
Ferrous Iron	160	not given.
Free Sulphuric Acid ...	30	14.0

Both these waters were quite without action on stainless steel though they attacked ordinary mild steel quite rapidly.

In addition, the examples given on pp. 190 and 194 of the persistence of passivity when the amount of copper or ferric sulphate was reduced considerably below the normally safe limit are also of considerable importance as they show that if, in the handling of such acid waters, the ratio of salt, producing the passivity, to acid is temporarily reduced to a figure normally unsafe, such reduction will not necessarily lead to any attack on the steel.

Hydrochloric Acid attacks stainless steel vigorously, the rate of attack depending on the strength of the acid. The following figures were obtained for a duration of attack of 24 hours :—

Strength of Acid.	Loss in mgm. per sq. cm. per hour.	
	Stainless Steel	Mild Steel.
Normal (10 %)	0.82	1.84
5N. (50 %)	5.00	6.80

After the attack of hydrochloric or sulphuric acid, the surface of stainless steel shows the remains of the original dendritic structure of the ingot. In pieces cut from a rolled bar, such as those used for the above tests, the "fibre" of the steel, parallel to the direction of rolling, is very evident after the samples have been attacked by the acid.

Sulphurous Acid also attacks stainless steel, possibly owing partly to the sulphuric acid which is practically always present in the commercial acid.

Nitric Acid. The action of nitric acid on stainless steel has some very interesting features. Ordinary stainless steel is attacked by this acid only when the latter is very dilute and then only at a slow rate. By suitably choosing the composition of the steel even this restricted range of attack may be prevented. It is obvious, therefore, that the use of stainless steel is likely to prove of great value in connection with the manufacture and transport of nitric acid. For this reason, the effect of varying conditions, on the rate of attack of this acid on stainless material will be considered in some detail.

If samples of stainless steel of typical composition be immersed for a few hours in nitric acid of various strengths, it will be found that the maximum rate of attack occurs with acid of about "normal" strength. Such acid is comparatively dilute; it contains, of course, 67 grams of the pure acid per litre and may be prepared by adding one part of concentrated acid (S.G. 1.42) to 15 parts of water. The actual rates of attack produced by acids of various strengths are shown in the results set out in Table XXIII and plotted in curve B, Fig. 84. These results were obtained on hardened and tempered samples of stainless steel containing 0.32 per cent. carbon and 12.2 per cent. chromium with acids varying in strength from one tenth "normal" (N/10) to five times "normal" (5N); the former contains one

part of strong acid in about 160 parts of water, the latter approximating one part strong acid to three parts water. For comparison the results obtained under the same conditions with samples of ordinary mild steel containing 0.35 per cent.

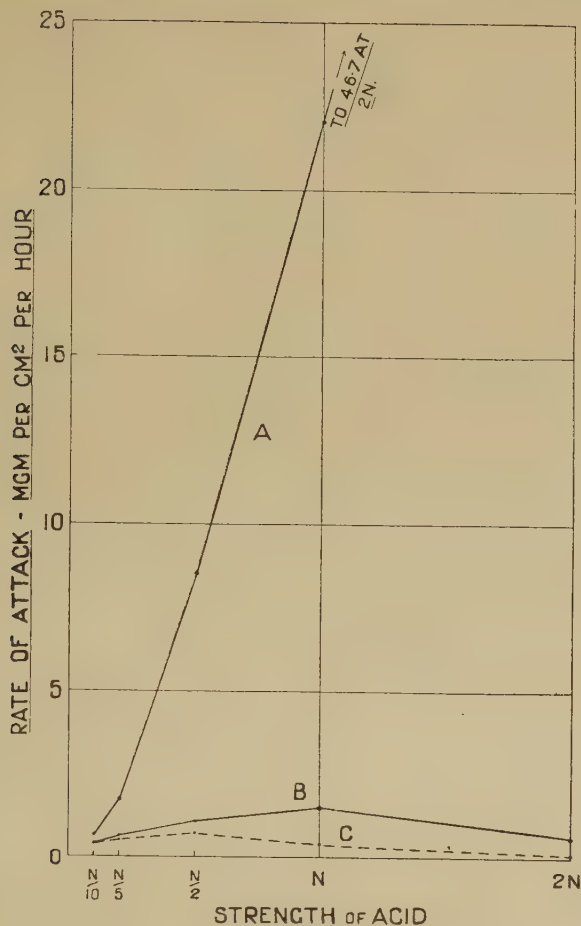


FIG. 84. Rate of attack of dilute nitric acid, of various strengths, on mild steel (curve A) and stainless steel (curve B, 5 hours attack; curve C, 24 hours attack).

carbon, 0.23 per cent. silicon and 0.71 manganese are included (curve A). The duration of attack was five hours in all cases except that of the 5N acid on the ordinary steel; owing to the violence of the attack in this case, the sample was left in the acid for 50 minutes only. The tests were carried out

at atmospheric temperature and in order to prevent an undue rise of temperature with the sample of mild steel in the 5N acid, the beaker containing this specimen was immersed in a larger vessel of water at atmospheric temperature.

TABLE XXIII

Rate of Attack of Nitric Acid of Various Strengths on Stainless Steel and Ordinary Mild Steel.

Strength of Acid.				Loss in milligrams per sq. cm. per hour.	
				Stainless Steel.	Mild Steel.
N/10	0.40	0.68
N/5	0.65	1.74
N/2	1.11	8.5
N.	1.53	22.1
2N.	0.61	46.7
5N.	0.01	about 600

The production of passivity in ordinary steel by the action of nitric acid stronger than that corresponding to a specific gravity of about 1.25 was referred to in the previous chapter (p. 153) where it was mentioned that when such steel was immersed in acid somewhat stronger than this, the metal was at first attacked but the rate of attack fell off rapidly and sometimes action ceased altogether. Passivity effects are similarly produced with stainless steel but with a much wider range of acid strength. With this steel, practically no attack is produced with acid of 5N strength (specific gravity about 1.20) and in the case of acids considerably weaker than this, the initial rate of attack very quickly falls off to zero. This may be illustrated by the figures given in Table XXIV. For the tests to which these refer, the samples used for the tests recorded in Table XXIII were re-polished and then re-tested in fresh acid for a period of twenty-four hours; a comparison of the figures thus obtained with those given by the previous attack lasting five hours is very interesting. As indicated in Table XXIV, which for convenience gives the results of both series of tests, the action of the acids of 2N and 5N strengths had ceased before the expiration of five hours while the rate of attack with

TABLE XXIV

Action of Nitric Acid on Stainless Steel.

Acid.	Loss in 5 hours' Attack.		Loss in 24 hours' Attack.	
	%	Mgm. per sq. cm. per hr.	%	Mgm. per sq. cm. per hr.
N/10.	0.102	0.40	0.430	0.355
N/5.	0.167	0.65	0.607	0.50
N/2	0.287	1.11	0.878	0.72
N.	0.395	1.53	0.481	0.395
2N.	0.154	0.61	0.140	0.115
5N.	0.003	0.01	0.003	0.002

acid of normal and semi-normal strengths fell off considerably in twenty-four hours and there was also a smaller diminution with N/5 acid. Owing to these effects the maximum average rate of attack in the 24 hours' test occurs at about semi-normal strength instead of normal (see also curve C, Fig. 84). It is very probable that with more prolonged periods, the production of passivity would become still more marked with the dilute solutions, so that the maximum average rate of attack over such long periods would approximate to that of N/5 or even N/10 acid rather than to that of N/2.

The production of passivity with prolonged attack of acid of normal strength is still more clearly shown by the results of the following experiment. Four similar samples of hardened and tempered stainless steel were placed in normal nitric acid for 3, 6, 24 and 72 hours respectively, with the following results :—

Duration of Attack.					Loss %	Average loss in mgm. per sq. cm. per hour.
3 hours	0.33	2.14
6 "	0.575	1.89
24 "	0.70	0.57
72 "	0.726	0.197

Assuming that the losses of the first three samples were substantially the same as those of the fourth during

the corresponding periods of the test, the losses of this sample during the several periods would be as set out below :—

Hours.	Loss %.	Average loss in mgm. per sq. cm. per hour during each separate period.
First three.	0.33	2.14
3 to 6	0.245	1.64
6 to 24	0.125	0.13
24 to 72	0.026	0.007

These figures are plotted in Fig. 85, which shows very strikingly how rapidly the rate of attack of this acid falls off as the duration of the test increases, so much so that after the sample has been immersed for about a day, action has almost ceased. If the samples are allowed to stay in

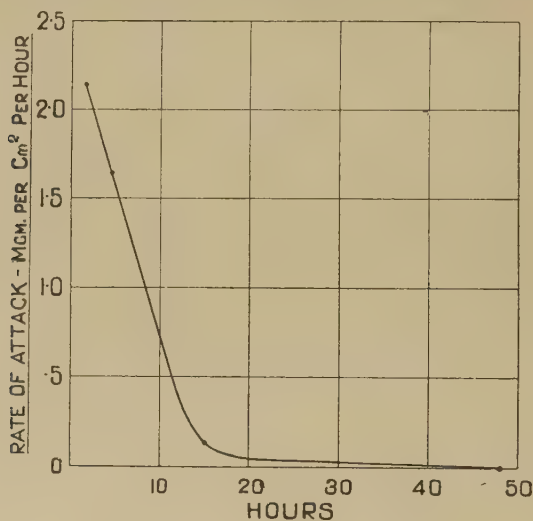


FIG. 85. Falling off in rate of attack of normal nitric acid on stainless steel with increasing duration of test.

the acid until action has practically ceased and are then taken out, washed and rubbed well, and then dried, they still retain their passivity although dry for comparatively long periods; thus samples so treated were found to be still completely passive to normal nitric acid after they had been kept for seven weeks.

Passivity is also produced if samples are taken out of the acid during the first few hours of immersion, while the attack is still progressing, and washed, rubbed and dried. If they are then immediately put back into the acid, no further action takes place. If such samples are allowed to remain dry, however, they lose their passivity during the course of a few hours.

The passivity produced in stainless steel by the action of nitric acid also retards the subsequent attack of dilute sulphuric or hydrochloric acids on the samples. The retardation, however, is only temporary, thus samples made passive by the prolonged action of normal nitric acid were subsequently placed in five per cent. sulphuric acid and were at first only very slowly attacked; the rate of attack however, gradually increased and after being in the sulphuric acid for three to four hours, the samples were being attacked at the normal rate. With ten per cent. hydrochloric acid, the passivity similarly disappeared in about two hours.

It is evident from the results given in the last few pages, that stainless steel is practically unattacked by nitric acid of 5N strength (specific gravity about 1.20). This also applies to all greater strengths of this acid. As acid of specific gravity 1.20 attacks ordinary steel very rapidly, this reagent is useful should stainless steel be accidentally mixed up with ordinary steel, because it affords a certain means of identifying the two types of steel. It may be mentioned in this respect that it is quite immaterial whether the stainless steel is in the hardened, hardened and tempered or annealed conditions, or whether it has been cold worked or not.

If samples of stainless steel are exposed for prolonged periods, e.g., lasting a month or six weeks, to nitric acid of 5N or greater strength, the surface of the steel is coloured a purplish tint, but there is no appreciable alteration in the weight of the sample. The colour thus produced bears some resemblance to a "temper colour" and is probably of a similar nature to the latter. It is also interesting to note that if a polished microsection be treated in this way, it is found that, although the back-ground of ferrite is coloured as described above, the particles of carbide remain brilliantly white. The effect thus produced is often strikingly beautiful and the method of etching would undoubtedly

be valuable microscopically if the time required to produce the effect were not so long.

Up to now, the action of nitric acid of various strengths has been discussed in relation to a typical stainless steel containing 0·32 per cent. carbon and 12·2 per cent. chromium; it is necessary however to consider, in addition, how the action of this acid is affected by variations in the chromium and carbon contents of the steel because experiment has shown that the composition of the steel has a marked effect on its resistance to the attack of dilute nitric acid.

The investigations of Monnartz* showed that the addition of chromium to iron greatly increased the resistance of this metal to nitric acid. His results with regard to alloys containing up to 20 per cent. chromium may be summarised as follows:—

(1) In the case of alloys containing up to 4 per cent. of chromium, the resistance to dilute nitric acid diminishes as the chromium increases. On the other hand the resistance to attack by concentrated nitric acid becomes greater.

(2) With alloys containing from 4 to 14 per cent. chromium, the resistance to dilute nitric acid increases very rapidly as the amount of chromium increases.

(3) As the chromium rises from 14 to 20 per cent., the resistance to dilute acid continues to increase slowly.

The author has not investigated the range up to four per cent. chromium, but the action of dilute nitric acid of “normal” strength and of the stronger acid of specific gravity 1·20, approximately 5N., on a series of low carbon steels containing chromium in amounts varying from 4·72 per cent. to 17·5 per cent. is indicated in Table XXV. A sample of mild steel free from chromium was included for comparison. The duration of attack in the case of the dilute acid was 5 hours. With the stronger acid, the attack was for 24 hours except in the case of the mild steel free from chromium; this sample was, of course, attacked extremely violently and was left in the acid for 20 minutes only. The losses are given in milligrams per square centimetre of

* *Metallurgie*. Vol. VIII. pp. 161-176, 193-201.

surface of the samples per hour and also as a percentage of the original weight of each sample.

TABLE XXV.

Effect of Chromium Content on the Action of Nitric Acid on Steel.

Composition of Steel.		" Normal " Acid.		S.G. 1.20 Acid.	
Carbon, %	Chromium, %	Loss % in 5 hours.	Mgm. per sq. cm. per hour.	Loss % in 24 hours.	Mgm. per sq. cm. per hour.
0.16	nil.	5.57	16.2	*39.9	about 1,250
0.14	4.72	4.95	15.65	2.0	1.64
0.12	6.2	4.60	13.5	0.082	0.064
0.09	7.5	2.07	6.15	0.006	0.005
0.16	10.0	0.785	2.1	† trace.	trace.
0.15	10.9	0.295	0.88	Nil.	Nil.
0.09	12.0	0.122	0.35	"	"
0.14	13.1	0.026	0.08	"	"
0.09	14.0	0.0097	0.03	"	"
0.10	15.5	Nil.	Nil.	"	"
0.13	17.5	"	"	"	"

The results indicate clearly the effect of a relatively small amount of chromium (4.72 per cent.) in retarding the attack of the stronger acid. With the dilute acid, the rate of attack falls rapidly when the chromium is raised above about six per cent.

The results with acids of normal strength on the steels with chromium content in the stainless range are plotted in Fig. 86, curve B. Curve A in the same diagram gives the results similarly obtained with a series of steels containing 0.31 per cent. to 0.33 per cent. carbon and varying amounts of chromium. The two curves indicate the differences produced by an increase of carbon of about 0.2 per cent. If the curves are examined it will be noted that similar rates of attack with the two series of steels are obtained when the chromium content in the lower carbon steels is approximately two per cent. lower than in the higher carbon series. Assuming,

* In 20 minutes only.

† Attack practically nil, the polished surface of the sample was only dulled after the attack to a barely perceptible amount.

as seems justifiable, that the resistance of the steel to the attack of nitric acid is due to the chromium in solid solution in the iron, and not to that existing as free carbide, it is interesting to note that this result is in agreement with the assumption previously made that the ratio of chromium to carbon in the carbide is approximately 10 to 1. It should be mentioned that in all the experiments described above, the steels were in the fully tempered condition.

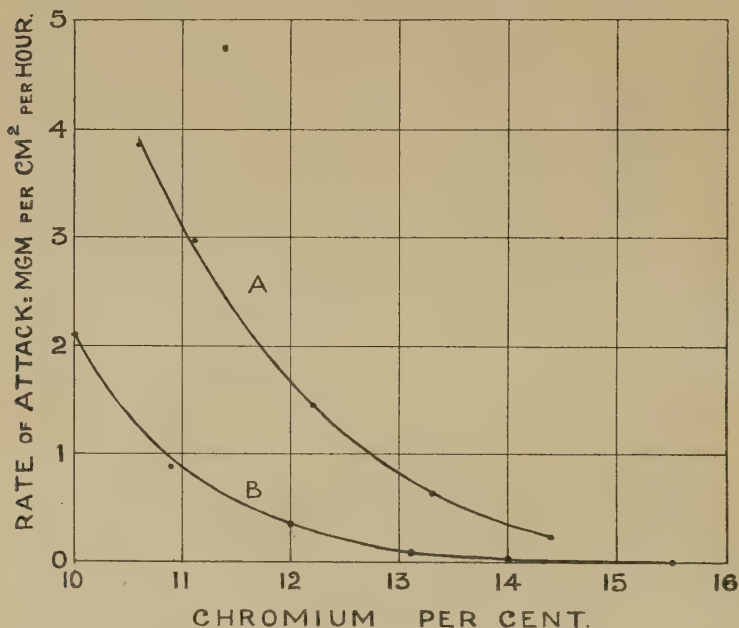


FIG. 86. Effect of chromium content on the rate of attack of normal nitric acid on stainless steel.

Curve A. Steels with 0.31/0.33 per cent. carbon.

„ B. „ „ 0.09/0.16 „ „ „

The table on page 203 shows that stainless iron containing 0.10 per cent. carbon and 15.5 per cent. chromium is unattacked by nitric acid of normal strength or of specific gravity 1.20; in addition, still stronger acid has no action on it. Further tests on this steel with acids ranging in strength from N/10 to 5N show that it is quite unattacked by nitric acid of any strength within these limits either at atmospheric temperature or at 80° to 85° C.

All the tests with nitric acid described up to now,

with the exception of that mentioned in the last paragraph, were carried out at atmospheric temperature. Further experiments in which the steel was exposed to the attack of the acid at 80° to 85° C. show that the rate of attack of "normal" nitric acid at this temperature is not greatly different from its rate of attack at ordinary temperatures providing the chromium content of the steel exceeds about 12 or 13 per cent. With steels containing less chromium than this, the rate of attack of acid of normal strength is greatly accelerated by the rise in temperature. With "5N" acid, only a very slight attack is produced even at 80°/85° C. For example, samples of the series of steels containing about 0.3 per cent. carbon which were used for the experiments on page 203, were attacked as indicated in Table XXVI when immersed in the acids for six hours at 80°/85° C.

TABLE XXVI

*Effect of Chromium Content on the Rate of Attack
of Nitric Acid at 80°/85° C.*

Composition of Steel.					Loss in mgm. per sq. cm. per hour		
No.					“ Normal ” Acid.	“ 5N ” Acid.	
A.	10.6	115	0.03
B.	11.1	16.5	—
C.	12.2	1.09	0.025
D.	13.3	0.41	0.01
E.	14.4	0.27	0.0055

These figures should be compared with those plotted in curve A, Fig. 86.

The effect of varying acid strength on the rate of attack of nitric acid at 80° to 85° C. is indicated by the results in Table XXVII obtained on steel C, Table XXVI, containing 0.32 per cent. carbon and 12.2 per cent. chromium with an attack lasting six hours.

A comparison of these results with those in Table XXIII (page 198), obtained on samples of the same steel, shows that the attack of very dilute nitric acid, up to about semi-normal strength, is greatly increased by raising the

temperature from atmospheric to 80°/85° C., but with acids of normal strength and upwards, the rate of attack is not greatly affected by the rise in temperature. It is obvious however from the results given on page 205 that the limiting strength of acid will depend on the amount of carbon and chromium in the steel.

TABLE XXVII

*Rate of Attack of Nitric Acid at 80°/85° C. on
Stainless Steel (12·2 per cent. Chromium).*

Strength of Acid.					Loss %.	Loss in mgm. per sq. cm. per hour.
N/10	1·50	4·90
N/5	2·69	8·82
N/2	4·56	15·13
N.	0·35	1·09
2N.	0·056	0·20
5N.	0·008	0·025

Summing up all the results obtained, one may conclude that an ordinary stainless steel containing 12 to 13 per cent. chromium and 0·3 per cent. carbon is practically immune from attack, at ordinary temperatures, by nitric acid of about 5N strength (specific gravity about 1·20) and upwards and is only slightly attacked by more dilute solutions of this acid. At higher temperatures, the rate of attack with very dilute acid increases considerably.

By increasing the chromium content or decreasing the carbon, the resistance to the attack of dilute nitric acid increases gradually, so that stainless iron with about 15 per cent. of chromium resists entirely the attack of all strengths of acid both at ordinary temperatures and at 80° to 85° C. It is obvious that such a material is likely to prove of great value to the nitric acid industry. A similar complete resistance to the attack of nitric acid is obtained with certain stainless steels containing large amounts of nickel; these are described in the next chapter.

It has been mentioned earlier that both copper and ferric nitrates retard the attack of dilute nitric acid on stain-

less steel and, if present in sufficient amount, prevent action altogether. Their action is thus similar to that of the corresponding sulphates on the attack of sulphuric acid. The extent of this action and the amount of each metal, present as nitrate, required to produce it is indicated in Fig. 87, in

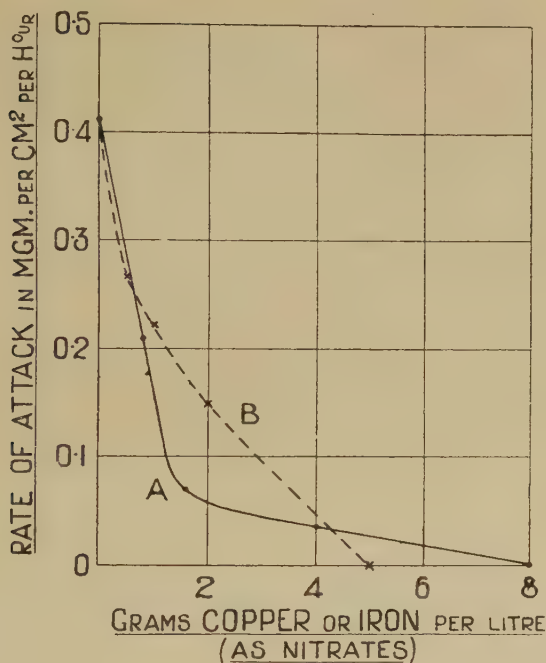


FIG. 87. Effect of copper nitrate and ferric nitrate on the rate of attack of normal nitric acid on stainless steel.

Curve A. Copper nitrate.

„ B. Ferric nitrate.

which are plotted the results obtained with acid of normal strength on hardened and tempered samples of steel containing 0.30 per cent. carbon and 12.6 per cent. chromium. The tests were carried out at atmospheric temperature and were of six hours' duration. As will be seen, the presence of eight grams of copper per litre or of five grams of iron per litre, both as nitrates, sufficed to prevent entirely the action of the acid on stainless steel.

The results with ferric nitrate are of importance in connection with the use of a bath containing about five per cent. of nitric acid for brightening up the surfaces of articles

previously pickled in the ordinary sulphuric acid pickling bath (see page 68). It is obvious that the gradual accumulation of ferric nitrate in the nitric acid bath will retard and finally prevent its action. As soon, therefore, as the amount of dissolved ferric nitrate becomes sufficient to cause appreciable retardation of the bath, the latter should not be further "revived" by the addition of fresh acid, but should be discarded entirely and a fresh bath made up.

Phosphoric Acid has a slow attack on stainless steel. Samples of the latter, containing 0.3 per cent. carbon and 12.6 per cent. chromium, and of mild steel, when exposed for 24 hours to solutions of various strength of this acid, were attacked as indicated below :—

Strength of Acid	Per cent. loss in weight.		Loss, mgm. per sq. cm. per hour.	
	Stainless Steel.	Mild Steel.	Stainless Steel.	Mild Steel.
5 % 0.067	1.51	0.050	1.11
25 % 0.27	3.56	0.20	2.60
66.3 % (S.G. 1.5)	... 0.66	6.19	0.47	4.62

Boric Acid. Samples of stainless steel immersed for seven days in a normal solution of this acid, containing 20.7 grams per litre, were quite unattacked.

Organic Acids. It was mentioned on page 184 that pure solutions of the acids present in fruit and other juices had a distinctly greater action on stainless steel than the natural juices. The following Table gives particulars of the action of various organic acids on stainless steel. Figures for mild steel obtained under the same conditions are included for comparison, and serve to indicate that in most cases where the stainless steel is attacked, the rate of attack is considerably less than that of mild steel under the same conditions.

In the case of tannic acid, the amount of iron dissolved from the mild steel appears to be quite small; actually, however, it was amply sufficient to turn the solution of the acid into a black inky fluid. In the case of the stainless steel, the acid solution appeared to be quite unaffected.

TABLE XXVIII

Action of Organic Acids on Stainless Steel and Ordinary Mild Steel at Atmospheric Temperature.

Acid.	Strength.	Duration of Attack.	Stainless Steel.		Mild Steel.	
			Loss %.	Loss, mgm. per sq. cm. per hour.	Loss %.	Loss, mgm. per sq. cm. per hour.
Acetic ...	5 %	14 days.	0.275	0.014	1.26	0.067
„ ...	15 %	„	0.23	0.012	1.92	0.105
„ ...	33 % (B.P.)	„	0.23	0.012	2.19	0.115
„ ...	Glacial.	„	No	action.	2.46	0.124
Carbolic	5 %	14 days.	No	action.	0.09	0.005
Citric ...	6 %	7 days.	0.107	0.011	2.48	0.260
Formic ...	10 %	12 days.	2.92	0.26	4.25	0.33
Oleic ...	Pure.	14 days.	No	action.	Not	tested.
Oxalic ...	Normal	10 days.	0.27	0.021	0.42	0.036
Tannic ...	10 %	14 days.	No	action.	0.078	0.0042
Tartaric ..	Normal.	14 days.	0.16	0.0085	1.17	0.062
„ ...	25 %	„	0.437	0.022	2.63	0.14

The samples used for the tests in carbolic acid were, after drying, weighing and examining, put back into the acid and the latter heated to 80° to 85°C., and kept at that temperature for 48 hours. The stainless steel was then still quite unattacked while the mild steel had lost weight at the rate of 0.21 milligrams per square centimetre per hour, corresponding to a loss of 0.55 per cent. in 48 hours.

With regard to oleic acid, the stainless steel sample was subsequently exposed for 14 days to the action of the acid at 60° C., and was then still quite unattacked.

Electrochemical Corrosion in Contact with Copper Alloys and Graphite. Both copper alloys and graphite are electronegative to stainless steel and, therefore, may set up corrosion in the steel when the latter is in contact with them in the presence of some electrolyte. Such corrosion

effects are less likely to take place in ordinary water than in electrolytes such as aqueous solutions of salts: in fact test samples of stainless steel have been immersed in water while in contact with brass, bronze and gun metal for several weeks with negligible effects on the steel. It is well, however, to realise that such corrosive effects may be produced and that also the liability of them occurring may be reduced very considerably by suitable modifications in the analysis of the steel. Increasing the chromium content of the steel lessens the possibility of action taking place so that where service conditions liable to give rise to such action have to be withstood, it is advisable to select steel containing as high a percentage of chromium as is consistent with the mechanical properties desired in the steel.

The importance of this limitation as regards mechanical properties will be recognised from the account given in Chapter IV of the properties of material containing 14 to 20 per cent. chromium. By suitable adjustment of the carbon content, however, steel with about 15 per cent. of chromium will give a range of mechanical properties suitable for many engineering purposes and such material is very resistant to the electrochemical action of copper alloys and is less likely to be attacked by graphite than the lower chromium steel. Use may also be made of the special chromium-nickel steels, described in the next chapter, which do not appear to be attacked at all under such conditions.

Superheated Steam. The results obtained with test samples placed in steam valves and also with actual boiler and steam pipe fittings, such as blow-off valves, steam trap valves, steam cocks, etc., show that stainless steel resists the action of steam remarkably well. It is also unaffected under such conditions by contact with the ordinary copper or nickel alloys used for such steam fittings. Examples of the results obtained by the use of stainless steel for the working parts of various steam fittings will be given in a later chapter dealing with some engineering applications of stainless steel. It will be of interest, however, to describe an experiment made for the purpose of testing the comparative resistance of stainless steel, ordinary steel and phosphor bronze to the erosive action of a steam jet. Small flat specimens of the three metals were held in a wooden frame,

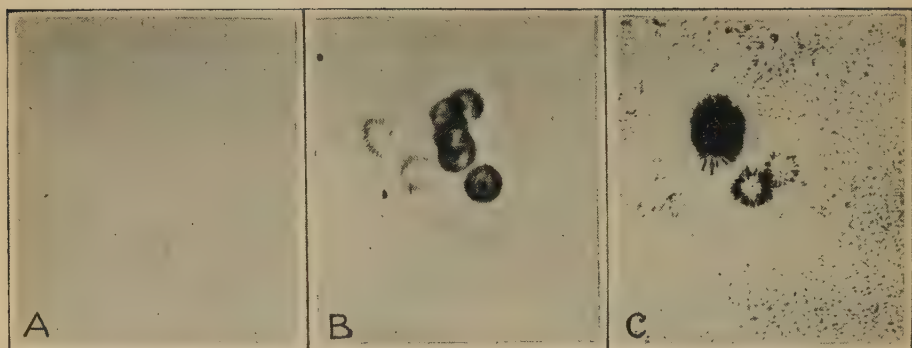


FIG. 88. Erosion tests with steam jet. (See page 210.)

- A. Hardened stainless steel.
- B. Chill cast phosphor bronze.
- C. Mild steel.

(The only effect on the stainless steel was a discolouration almost too slight to reproduce. The multiple pits in B and C are due to accidental movement of the specimens during the course of the experiment.)

To face page 211].

each specimen $\frac{1}{8}$ -inch from a jet, $\frac{1}{16}$ -inch in diameter. Steam was blown through the jets at a pressure of 120 lbs. per square inch. The exposure was 200 hours in each case. The appearance of the three samples at the conclusion of the test is shown in Fig. 88. The stainless steel specimen, which was in the hardened condition, was practically unattacked, the only effect being a slight discoloration almost too slight to reproduce. On the other hand, the samples of ordinary steel and of phosphor bronze were deeply eroded where the jets of steam had impinged on them.

For the purpose of testing the effect of copper and other alloys on stainless steel when the two are exposed, in contact with each other, to the action of steam, small samples of stainless steel were tightly embedded in pieces of each of the following alloys* :—

	Percentage Composition.					
	Copper.	Tin.	Zinc.	Lead.	Nickel.	Antimony.
Gun Metal	88	10	2	—	—	—
Copper Nickel Alloy.	53	8.5	9	14	14	1.5
Metallic Packing ...	—	20	—	65	—	15

The duplex samples were exposed, in a steampipe, to the action of steam at 360° F. during a period of three weeks. During each week the boilers were working for four days and were shut down during the week-ends. The samples were thus exposed for twelve days to the action of the hot steam and during the three week-ends (nine days in all) to the damp atmosphere of the comparatively cold pipe. At the end of the period the stainless steel samples were only stained to a dark straw tint, similar to a temper colour. Both the gun metal and the nickel alloy were stained more than the stainless steel while the metallic packing was distinctly attacked, producing an etched surface.

* The duplex samples were prepared in the following manner. A hole was drilled in a disc of the alloy and a piece of stainless steel, machined to a driving fit in the hole, was driven into this. By this means metallic contact between the alloy and stainless steel was obtained.

Lubricating Oils, greases, paraffin, benzol, and petrol, do not appear to have the slightest action on stainless steel.

Oxidation at High Temperatures. A polished sample of stainless steel on being gradually heated assumes a series of temper colours similar to those produced on ordinary steel but at considerably higher temperatures than with the latter material; thus the colours noted below were obtained on polished samples of hardened stainless steel heated to the temperatures indicated:—

Temperature.	Temper colour.
300° C. Pale Straw.
350° C. Brownish Straw.
400° C. Brownish Purple.
450° C. Bluish Purple.
500° C. Reddish Purple.
550° C. Purple Blue.
600° C. Light Blue.
650° C. Bluish Violet
700° C. Greyish Violet.
750° C. Grey.

Such tints are known to be due to very thin oxide films. After being heated in the range 750° C. to about 825° C., a polished surface of stainless steel becomes covered with a thin grey film without, however, losing its polished appearance and the sample neither gains nor loses weight appreciably. Above 825° C. stainless steel or iron begins to scale appreciably.

The comparative behaviour of stainless steel and other types of steel on prolonged heating at high temperatures is illustrated in Fig. 89. In this experiment, samples of the various steels, in the form of cylinders about $\frac{5}{8}$ -ins. diameter and weighing 60 grams, were heated together in a gas-fired oven furnace. The temperature of the furnace was raised after definite periods of time as shown in the diagram. At the end of each 24 hours, the samples were drawn from the furnace and after the loosely adherent scale had been removed, were weighed. The loss in weight is shown as a percentage of the original weight. It will be seen that after seven days soaking in the range 700° C. to 825° C. the sample of stainless steel had hardly altered in

weight, the actual loss being 0.25 per cent. On the other hand, the mild carbon steel and the ordinary types of structural alloy steels had lost amounts varying from 17 to 22 per cent. of their weight after the same treatment. The high-speed steel lost 7.1 per cent. of its weight while the 25 per cent. nickel steel, which most nearly approached the stainless steel lost 2.6 per cent.

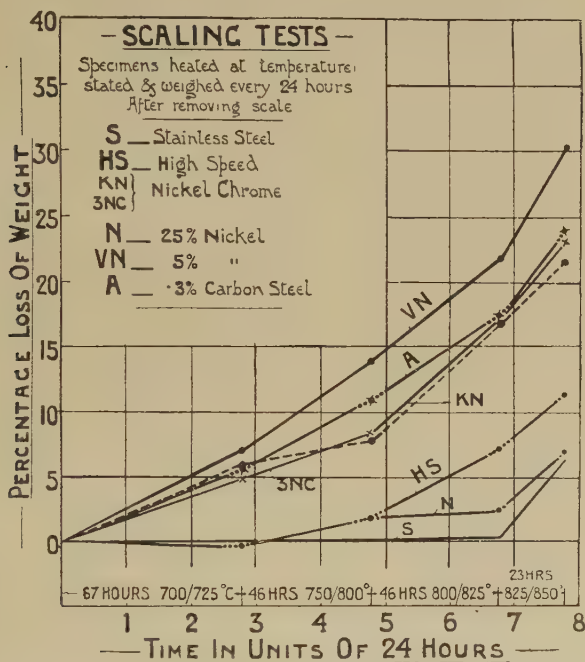


FIG. 89. Scaling tests on stainless and other steels.

Above 825°C., as will be seen from Fig. 89, the rate of scaling of stainless steel increases somewhat rapidly. The onset of this comparatively rapid scaling may, however, be delayed until higher temperatures are reached by the addition of other metals, the most effective of which are silicon and aluminium, or by raising the chromium content considerably. Some consideration of the properties of the chromium-silicon steels will be given in the next chapter.

As an indication of the effect of aluminium, the following results are of interest. Cylinders, about one inch

long and $1\frac{1}{4}$ -inch diameter of two samples of stainless iron containing respectively :—

			Carbon %	Silicon %	Chromium %	Aluminium %
A.	0.10	0.22	11.9	Nil.
B.	0.11	0.58	12.0	1.54

were heated for $4\frac{1}{2}$ hours, in a gas-fired oven furnace, in the range 910° to 950°C . They were then withdrawn and cooled. Sample 'A' had scaled appreciably and, after the loosely adherent scale had been removed, was found to have lost 3.0 per cent. of its original weight. Sample B, on the other hand, was only slightly tarnished and practically unaltered in weight. The samples were then replaced in the muffle and the latter kept in the range 950° to $1,025^{\circ}\text{C}$. for 18 hours. On removing from the furnace and cooling, both samples were found to have scaled appreciably but, while the loss on sample A amounted to 9.9 per cent. of its weight, that on B was only 4.0 per cent. It is obvious, therefore, that the presence of about one-and-a-half per cent. of aluminium raises the temperature at which scaling becomes appreciable to about 950°C .

Increasing the chromium content up to 20 per cent. or more also brings about a very decided increase in resistance to oxidation at high temperatures. As an example of this, the results obtained in an experiment in which a series of such high chromium steels were heated in a gas-fired oven furnace at 950° to $1,025^{\circ}\text{C}$. for ten days are of interest. The samples were one-and-a-half inches long and seven-eighths of an inch in diameter, and, after being heated as described above, had gained in weight to the extent shown below :—

No.	Composition.		Gain in weight per cent.	Type of Scale.
	Carbon %	Chromium %		
A.	0.23	19.9	0.315	Thin adherent black scale.
B.	0.23	24.8	0.03	Very thin greenish black scale.
C.	0.24	28.1	0.01	Very thin adherent greenish scale.
D.	0.19	33.4	0.02	

The alloys with 30 per cent. or so of chromium are extremely resistant even at considerably higher temperatures. Thus a further sample of alloy D was heated in a gas-fired furnace for 20 days at $1,000^{\circ}\text{C.} (\pm 25^{\circ}\text{C.})$ and then for four days at $1,100^{\circ}\text{C.}$ At the end of this treatment, the sample was coated with a light greenish skin and had lost only 0.53 per cent. of its weight. To give some idea as to the degree of resistance implied by these figures, it may be mentioned that a piece of ordinary mild steel of similar size, which was placed in the furnace beside the high chromium alloy for the first three days (at $1,000^{\circ}\text{C.} \pm 25^{\circ}$) only, lost in that period 45 per cent. of its weight by scaling.

The resistance to oxidation at high temperatures of such high chromium alloys was pointed out by F. M. Becket who took out a patent* in regard to their use for such purposes. A good description of some of the properties of such high chromium alloys was given by C. E. MacQuigg in a paper† entitled "Some Commercial Alloys of Iron, Chromium and Carbon in the Higher Chromium Ranges," to which those interested in such alloys may be referred.

* U.S.A. Patent No. 1,245,552. Nov., 1917.

† Trans. Amer. Inst. Min. and Met., Eng. August, 1923.

SPECIAL STAINLESS STEELS

CHAPTER VII

SPECIAL STAINLESS STEELS

The greater part of the stainless material manufactured and used at the present time is made in accordance with the specification laid down by the inventor in 1915. During the period which has elapsed since then, developments have undoubtedly taken place, but they have been mainly on the lines of producing several standardised types of the steel, the composition of each being adjusted within certain sets of more or less narrow limits, in order that the physical or non-corrosive properties of each type should be most suitable for certain specified purposes. This standardisation is most noticeably seen in regard to the carbon content of the steel. As already stated, it quickly became evident to those who were interested in the development of the material, that stainless steel should be regarded as a series of steels, the carbon content of each member of the series being adjusted to suit the particular purpose for which it was to be used in precisely the same way that the carbon content of ordinary steel varies according to whether it is to be made into an axle or a tyre, a shovel or a spring, a piece of shafting or a turning tool. This aspect of the case became especially noticeable, of course, when the opportunity arose for developing the use of the steel for various engineering purposes and the necessity for adjusting the carbon content to suit varying engineering requirements has been given detailed consideration in the previous chapters.

Further experience in the use of the steel has also indicated the desirability, in certain special cases, of modifying its chromium content. Occasions when such modifications are desirable may arise from considerations of an economic nature or from the necessity, which is sometimes present, of effecting a compromise between the requirements in regard to the physical properties of the material on the one hand

and, on the other hand, its capability of resisting, to an enhanced degree, certain types of corrosion.

It has been shown in the preceding pages that the resistance of the steel to general corrosion increases with the amount of chromium which it contains, so that in certain cases where resistance to severely corrosive conditions is desirable, raising the chromium content to 16 or even 20 per cent. would obviously be an advantage. On the other hand, it has also been shown that the physical properties of such high chromium alloys are not always of the most desirable type, this being especially noticeable in the fact that these alloys, unless high in carbon, possess little or no capacity for hardening. It is obvious, therefore, that the selection of the most suitable analysis for specific purposes will often be in the nature of a compromise and that the chromium content securing the best combination of physical and non-corrosive requirements may and probably will vary in different cases. This may be illustrated by considering two extreme cases. In the use of stainless steel for cutlery purposes, it is essential that the material shall be capable of hardening to a sufficient extent to function as a useful knife. However resistant to corrosion a knife may be, its use is obviously limited if its cutting powers are no greater than those of a butter knife or a silver fruit knife. To be successful it should also possess, when in a suitably hardened condition, sufficient surface stability to resist successfully the attack of such media as it is likely to come in contact with in the course of its every-day use. On the other hand, there is no necessity for it to possess such extreme resistance to corrosion as would be required to withstand, when in the fully tempered condition, such conditions as, for example, the electro-chemical action liable to be set up when the steel is in contact with copper alloys or graphite while immersed in an electrolyte such as brine ! For such cutlery purposes a chromium content of about 12 per cent. gives ample resistance to corrosion and enables the cutler to produce a knife of sufficient hardness to be worthy of the name.

Increasing the chromium to 14 or 15 per cent. undoubtedly gives greater resistance to general corrosion, but to what purpose ? If, as is definitely the case, material with about 12 per cent. has ample resistance for all cutlery

requirements, why give it more, especially as by so doing the capacity of the steel for hardening becomes less and, in addition, distinctly higher quenching temperatures, with their attendant difficulties of increased scaling, greater liability of cracking and coarser structure in the hardened knife, are required to produce the maximum hardness the material is capable of giving?

Actually cutlery, which will have adequate resistance to corrosion to function as truly "stainless" cutlery, can be manufactured from material containing considerably less than 12 per cent. chromium while, at the same time, the knives made from such material possess a hardness and "springiness" superior to that of knives containing 12 per cent. or so of chromium and practically equal to that which one associates with blades manufactured from first-class shear steel. The author has had a table-knife made from material containing 8.6 per cent. chromium in daily use for the past ten months. It has never been cleaned or sharpened and is still in perfect condition, while it possesses a "springiness" which would be a revelation to those accustomed to the very high chromium article. Such lower chromium material probably requires more care on the part of the cutler in producing a stainless knife. Thus, in order that it may be truly stainless, it will need to be hardened from a higher temperature than that required for the steel containing about 12 per cent. of chromium and it is more likely to suffer through careless grinding. Probably, therefore, the cutler will prefer to use the higher chromium material containing about 12 per cent. or so of that element; certainly this material is, from his point of view, more "fool-proof" than the other. Such a consideration, both as regards manufacture of the steel and of the knife, may be the underlying idea in the suggested use of the very high chromium material, containing 14 or 15 per cent. of that metal, for cutlery.

At the other extreme, one may consider the case of material to be used for ornamental work or for articles which require no great mechanical strength in the material from which they are made but which should possess, in as great a degree as possible, resistance to general corrosion. As such articles have frequently to be machined, pressed, or otherwise cold-worked in the course of their manufacture,

it is desirable that this exceptionally good resistance to corrosion should be possessed by the material when it is in its softest condition. For such purposes, as high a chromium content as economic conditions will allow is desirable in the material.

Such developments as have been indicated above, however, may be regarded simply as splitting up the original range of composition specified by the inventor into a series of sub-ranges for special purposes except that, as suggested in the last paragraph, they may have led to the use of steels with a chromium content greater than that, actually 16 per cent., which he had in mind. Technical knowledge, however, is never stationary although its rate of progress often varies considerably. Further developments which have taken place, more especially during the last three or four years, suggest that the position indicated above does not by any means represent finality as regards the production of stainless material. Experience has indicated that even with such developments and modifications as are described above, the range of properties, physical and non-corrosive, obtainable from such stainless steels is not sufficient to meet all engineering requirements and, for some considerable time, experiments have been in progress to see if it were possible, by the addition of other alloying elements to stainless steel, to develop to an enhanced degree certain properties possessed by the material or to induce in it others, more especially in the nature of resistance to the attack of specially corrosive media, which previously it did not possess in any noticeable degree. The superior properties made available by the use of alloy steels in comparison with ordinary carbon steels suggest at once the possibility of regarding stainless steel as a sort of base and of constructing on it a series of "alloyed" stainless steels having particular properties specially developed just as the ordinary constructional alloy steels are developed from mild carbon steel as a base. Such work is, as yet, only in its infancy, but already a considerable measure of success has been achieved in the production of alloys which possess an enhanced resistance to particular types of corrosion. As frequently happens with other alloys, however, the development of these special properties is often accompanied by loss in respect of others.

Various metals have been suggested for adding to

stainless steel for the purpose of modifying its properties and of such metals most work has been done with silicon and nickel. Copper has also been suggested as an addition producing a decided increase in acid resistance, for many purposes a very desirable effect. Very little has been done with the commercial development of such copper-chromium steels however, possibly because an even greater degree of acid resistance can be obtained by other means, e.g., by the addition of molybdenum or of comparatively large amounts of nickel. Among other metals, cobalt and tungsten have been suggested as additions producing valuable types of alloys, but little has been published with regard to the alloys so produced, except that cobalt-chromium steels have been recommended as being superior to plain chromium steels for the production of valves for internal combustion engines. However, in this case, there seems to be some doubt as to whether the claims made for the special alloy are fully justified.*

The effect of copper has been considered in previous chapters and some consideration will be given in the following pages to the chromium-silicon, chromium-molybdenum and chromium-nickel steels. The other alloys, however, are not sufficiently developed to merit further consideration than the short note given above.

A. CHROMIUM-SILICON STEELS. The influence of silicon on the properties of stainless steel has been indicated in some detail in Chapters IV and V. The greatest commercial value of the chromium-silicon alloys, relative to the plain chromium steels, appears to lie in their superior resistance to oxidation at high temperatures and for this reason they have found use for such a purpose as exhaust valves of internal combustion engines where temperatures of 800° C. and over are liable to be reached. In this particular case they have also the added advantage that, owing to the presence of the silicon, their carbon change point occurs at a higher temperature than in the plain chromium steels and therefore they are less liable to reach, in service, a temperature from which they would harden on cooling more or less rapidly. Obviously, if a valve reaches such a temperature

* See "Valve Steels for Internal Combustion Engines." Aitchison. Proc. Inst. Auto. Eng., Vol. XIV (1919), p. 31.

in use, it is likely to harden on cooling when the engine is stopped. On restarting the engine after it has become cold, there is a possibility that a valve so hardened may break. Examples of valve failures due to this cause were quoted by Aitchison in the paper mentioned above, though it is probable that they occur only very rarely.

For such purposes as this it is not necessary to use so high a chromium content as that in ordinary stainless steel; 6 to 8 per cent. is ample and this amount, in combination with about 1 per cent. of silicon and 0.5 per cent. of carbon gives a material which may be used up to about 850° C. while at the same time it possesses very good physical properties. The latter point is illustrated by the following tests obtained from bars, $1\frac{1}{8}$ inches in diameter, made from different casts of steel having approximately the above analysis:—

Cast.	Treatment.	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elonga- tion % on 2 ins.	Reduc- tion of Area %	Brinell Hard- ness No.	Izod Impact, ft. lbs.
A.	A.H. 900°, W.Q. 750°C.	40.8	52.6	28.0	61.5	251	49, 47, 44.
B.	" "	40.8	52.0	28.0	66.8	255	61, 60, 53.
C.	W.Q. 700°C.	44.8	58.2	22.0	49.7	286	29, 29, 24.
D.	W.Q. 750°C.	46.0	54.6	23.0	53.4	262	49, 40.
	W.Q. 700°C.	52.0	57.8	25.0	55.8	269	35, 30.
	W.Q. 750°C.	40.4	53.8	25.0	57.0	255	57, 85, 51.

If resistance to oxidation at still higher temperatures is required, the silicon content of the steel may be increased to 2 or 3 per cent., the chromium remaining at about 8 per cent. Material having such an analysis is very resistant to oxidation at any temperature up to about 1000° C.; in addition, it is not capable of being hardened by rapid cooling until a temperature nearly as high as this is reached. This is illustrated by the curves in Fig. 90, which show the Brinell hardness numbers obtained both on water quenching and air cooling small samples of such a steel from a series of gradually increasing temperatures. These curves also illustrate very strikingly the effect of silicon in reducing the air-hardening capacity of the steel to which it is added. With such a high silicon content, however, the effect of this element on the mechanical properties of the steel becomes very evident. Such steels, when hardened and fully tempered, are considerably harder than steels free from silicon

but otherwise similar in analysis; they also give low Izod impact values. Thus a bar of the following analysis:—

Carbon %	Silicon %	Manganese %	Chromium %
0·51	3·17	0·84	8·0

after being oil-hardened from 1000° C., followed by tempering at 800° C., gave the following tests:—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
50·4	62·8	22·0	40·6	293	8, 8, 8.

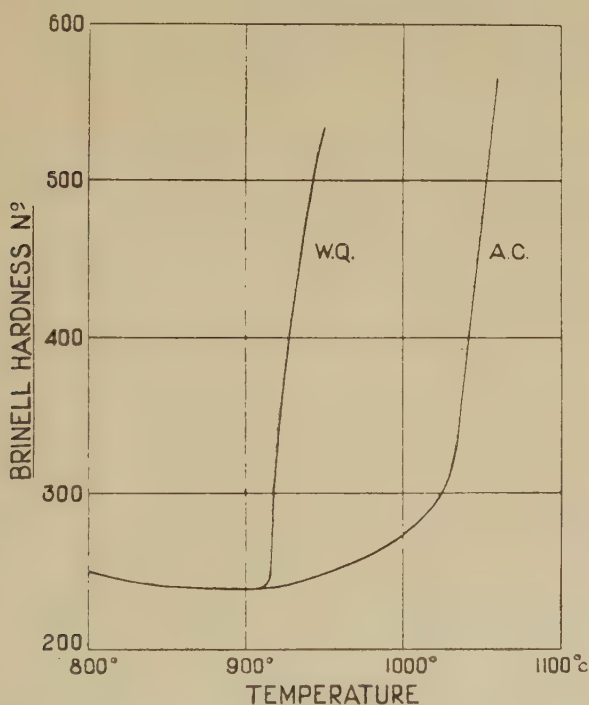


FIG. 90. Brinell hardness numbers obtained from small samples of steel containing 0·43 % carbon, 3·29 % silicon, 0·24 % manganese and 7·4 % chromium after water quenching (W.Q.) or air cooling (A.C.) from the temperatures indicated.

These values should be compared with those given by the lower silicon alloy mentioned earlier and also by stainless steel of similar carbon content, see p. 86.

The mechanical tests on these high silicon steels have been given for the sake of completeness. It does not necessarily follow, however, that the use of the material containing 2 or 3 per cent. of silicon for the manufacture of valves is to be deprecated because it has such a low impact value at ordinary temperatures. Large numbers of valves made of such steel and also of other types possessing equally low impact values, have been put into service during the last ten years or so and a broken valve is an exceedingly rare occurrence!

Such chromium-silicon steels as those described above do not resist oxidation at temperatures as high as do the nickel-chromium alloys of the "nichrome" type; they are, however, very much cheaper than the latter type of alloy and are more easily worked and will obviously be of value where the heat resistance which they possess is ample for the purpose required.

B. CHROMIUM-NICKEL STEELS. It has already been shown in Chapter IV that if sufficient nickel is added to a high chromium steel, an austenitic alloy is obtained. Such austenitic steels possess some very desirable properties and although they have the disadvantage that they cannot be hardened except by cold work, they are likely to prove exceedingly useful for a variety of purposes. Such alloys may contain an amount of chromium about equal to the upper limit specified for ordinary stainless steel (15 or 16 per cent.) or for certain purposes a still higher chromium content, about 20 per cent., may be used. The nickel content will be about 10 per cent. in the former case and about 7 per cent. in the latter. Such alloys are sold under various trade names, of which "Anka" (Messrs. Brown, Bayley's Steel Works, Ltd.), "Staybrite" (Messrs. Thos. Firth & Sons, Ltd.) and "V.2.A." (Messrs. Fried. Krupp) may be mentioned.

The non-corrosive properties of these high chromium-nickel alloys appear to have been studied in the first place in the Research Laboratory at Krupp's and it is interesting to note that the account published by Drs. Strauss and Maurer

of the properties of these alloys* suggests that they approached the study of them by the addition of chromium to nickel alloys rather than vice versa. In 1913, patents covering the manufacture of two series of chromium-nickel alloys were taken out in England and other countries by Clement Pasel and are held by Krupps. The two British patents (Nos. 13414 and 13415, 1913) apply respectively to alloys resistant to general corrosion (not acids) and to alloys resistant to the attack of acids, nitric acid being especially mentioned. In the first series, for resistance to general corrosion, the patent covered the use of alloys containing 0.5 to 20.0 per cent. nickel and 7.0 to 25 per cent. chromium and the production of both martensitic and austenitic types of steel was specifically mentioned. The second series, for resistance to acids, was entirely austenitic and comprised alloys included on the range 4 to 20 per cent. nickel and 15 to 40 per cent. chromium. In both series the carbon was limited to 1 per cent. In both patents, the methods of treatment necessary to secure workable and machinable material were specified. In passing, it may be mentioned that the British rights for the manufacture of these alloys are now held by the Firth-Brearley Stainless Steel Syndicate, under whose license the two Sheffield firms mentioned on p. 226 produce their respective products.

It is interesting to note that stainless steels which contain 0.5 per cent. or more nickel fall in the range of composition covered by the first patent mentioned above. Krupps, however, apparently regarded the presence of the nickel as being essential and they do not appear to have been aware that the non-corrosive properties were possessed by a pure chromium steel. Krupps have indeed manufactured during the last few years a steel, which they term "V.I.M.", similar to a stainless steel of cutlery temper but containing as an essential constituent 1.5 or 2.0 per cent. of nickel. As has been shown earlier, the presence of this nickel has little effect on the resistance to corrosion, though it affects the heat treatment of the steel in a marked degree and in a manner which is not always advantageous. Drs. Strauss and Maurer also appear to be under a curious misapprehension with regard to the hardening capacity of such a steel as this.

* Die Hochlegierten Chromnickelstähle als Nichtrostende Stähle. Strauss and Maurer. Kruppsche Monatshefte. August, 1920.

In the paper previously referred to, they state that such a steel, containing 0.21 per cent. carbon, 10.0 per cent. chromium, and 1.74 per cent. nickel, is what they call a "self-hardening" steel, as distinct from an "air-hardening" steel, in that the carbon change point always occurs on cooling at 280° C., no matter what the speed of cooling may be. Such a "self-hardening" steel could not be annealed because no matter how slowly cooled, it would always be martensitic. The experiments described on pp. 124 and 125 show, however, that if such a steel be cooled at a sufficiently slow rate, the A_{c1} point will occur in the range 600° to 700° C. and the steel become annealed. From the descriptions which Strauss and Maurer give of their experiments on the possibility of annealing this type of steel, it would appear that their inability to obtain the annealed condition arose from the fact that they did not cool the steel sufficiently slowly.

As a result of his investigations on these austenitic nickel-chromium steels, investigations carried out over a period of several years and to a large extent independently of the work of Krupps', the author believes that an alloy containing 15 or 16 per cent. chromium and 10 or 11 per cent. nickel possesses the best all-round combination of properties, and hence this is the type of alloy made, under the name "Anka," by the firm with which he is associated. There is actually little difference between the corrosion resisting properties of this steel and the Krupp type ("V.2.A.") containing about 20 per cent. chromium and 7 per cent. nickel, except that the lower chromium alloy is distinctly the more resistant to the attack of sulphuric and hydrochloric acids at atmospheric temperature. The "Staybrite" alloy made by Messrs. Thos. Firth & Sons, Ltd., is intermediate in composition between the "Anka" and "V.2.A." types.

(a) **Mechanical Properties.** From Strauss and Maurer's diagram, Fig. 65, page 127, it will be seen that, for the production of a completely austenitic steel, about 8 per cent. nickel is required with 15 per cent. chromium and about 6 per cent. nickel with 20 per cent. chromium; but, in the author's opinion, these amounts of nickel are somewhat low for the purpose. Alloys with the compositions given above would almost certainly harden appreciably after reheating to temperatures in the range 800° to 950° C.

(as indicated by curve A, Fig. 68) though they would become completely austenitic after reheating to 1000° C. or over.

The completely austenitic material is extremely tough and ductile; its tensile strength depends on its composition and on the mechanical and thermal treatment it has had. It cannot, of course, be hardened by heat treatment; hardening is only possible by some form of mechanical work but, after being so hardened, it may be softened by suitable treatment. All such steels are in their softest and most ductile condition after being reheated to 1000°/1100° C., followed by water quenching or air cooling, and the range of properties obtainable in such a condition by suitable variations in composition are illustrated by the following tests obtained on two such steels:—

Steel.	Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
A.	19.1	38.9	70.0	72.6	137	105, 107, 109
B.	16.4	58.9	57.0	51.0	163	119, 115, 120

Both these tests were obtained from bars $1\frac{1}{8}$ inches diameter (rolled from ingots 12 inches square), which had been quenched in water from 1000° C. prior to testing. The two steels had the following analyses:—

Steel	Carbon %	Silicon %	Manganese %	Chromium %	Nickel %
A.	0.10	0.25	0.24	15.2	11.4
B.	0.10	1.34	0.22	15.0	9.0

so that the higher tensile strength of steel B is presumably due, at least in part, to the presence of the silicon; incidentally, it may be noted that this silicon content has not had any bad effect on the impact value of the steel. The carbon content of these austenitic alloys has not such a marked influence on their mechanical properties as it has on those of the ordinary stainless steel, but it should preferably be kept low if soft ductile material is required. It should

also be noted that the hardness of these austenitic alloys increases with increasing content of chromium; this is illustrated by the following tests obtained from bars which had been fully softened :—

Steel.	Carbon %	Silicon %	Man- gane- se %	Chro- mium %	Nickel %	Yield Point, tons per sq. inch	Max. Stress, tons per sq. inch	Elonga- tion % on 2 ins	Reduc- tion of Area %	Brinell Hard- ness No.	Izod Impact, ft. lbs.
C.	0·21	0·36	0·18	15·4	10·3	18·8	45·7	64·0	67·8	163	112, 115, 120.
D.	0·24	0·26	0·29	20·2	8·4	27·0	53·0	59·0	51·4	185	118, 120, 120.

All these tests, in common with those from other austenitic steels, show a low value for the yield point and a very high value for elongation per cent., the greater part of the latter being produced by the general extension of the whole test piece and only a small amount by the localised extension due to the “neck.” The steels are also extremely tough under the impact test, a feature not always found in austenitic steels.

(b) **Forging and Rolling.** Steels such as these may be rolled and forged in much the same way as ordinary stainless steel. They are somewhat harder to work than the cutlery temper of the latter quality, because, as will be seen later, they retain their strength better at high temperatures. Forging or rolling may be continued down to about 900° C., 1100° C. being a suitable reheating temperature, without unduly hardening the steel by the mechanical work, but if these operations are continued below this temperature the steel not only becomes hard to work but also has its tensile strength, when cold, raised considerably. As an indication of the results obtainable on material rolled in the manner recommended above, the following tests were obtained from rolled bars, which were not subsequently treated in any way, of the steels described earlier :—

Steel.	Size of Bar.	Yield Point, tons per sq. inch.	Max. Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
A.	1½"	28·0	43·6	51·0	67·8	202	112, 114.
B.	1½"	26·8	68·0	43·0	49·7	212	120, 120.
„	¾"	33·4	70·7	45·0	59·7	241	120, 120.
C.	1"	36·5	54·7	43·0	55·8	—	100, 110, 115.
D.	1"	43·8	59·8	37·3	53·0	248	74, 71, 58.

These results indicate that in the rolled or forged condition the material has a tensile strength some five or ten tons per square inch higher than in the fully softened condition; in addition, the yield point is raised considerably in the worked material, while the ductility and toughness figures are exceedingly good.

It may be mentioned that no difficulty was experienced in machining the test pieces for any of these materials.*

The tests given above were obtained from bars of small size; very similar properties are, however, obtainable from bars or forgings of considerably greater size except, of course, that the hardening effect due to mechanical work is relatively less as a general rule in the larger-sized pieces. For example, the following figures were obtained from a bar, of similar analysis to C above, five feet long and five-and-a-quarter inches diameter in the "as rolled" condition:—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Izod Impact, ft. lbs.
22.0	40.0	52.0	63.7	83, 84, 83

On the other hand, as illustrating the effect of continuing the forging or rolling operation to lower temperatures than suggested above, a bar three-quarters of an inch diameter of similar material was rolled from the same initial reheating temperature, 1100° C., but the rolling continued until the temperature had fallen to about 600° C. Such a treatment is a type of cold work and during the last few passes of the rolling the bar was very hard and springy. In this condition the bar gave the following tests:—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on two inches.	Reduction of Area per cent.	Brinell Hardness No.	Izod Impact, ft. lbs.
49.2	85.3	37.5	38.3	321	80, 72, 84

* See page 284 with regard to the machining of these austenitic alloys.

Such a test is really remarkable; the impact value is particularly high, indicating that the material is tough even when severely work-hardened. The working of the steel at such a low red heat is not advisable, however, as the material is liable to split when forcibly distorted in such a manner.

In all the tests given for this austenitic steel, it will be noted that the ratio of the maximum stress to the Brinell hardness number differs appreciably from that found for ordinary stainless steel or for the general run of carbon or alloy steels. For these, the ratio has a value varying between 0.22 and 0.24. For the austenitic steel, as with other types of such steels, it is much higher, sometimes reaching a value of 0.35; in addition, its value varies more than with ordinary steels. Consequently, the Brinell hardness number should be used with caution in estimating the tensile strength of these steels. If the ordinary conversion figures applicable to most steels are used, the calculated value of the tensile strength so found from the Brinell hardness number will be less than that actually obtained from a tensile test by an amount which varies with the condition of the steel. As a general rule, the difference is greater when the material is in its softest condition and less when it is more or less work-hardened; it is also likely to be greater with a steel which contains barely sufficient nickel to be austenitic, that is, one which hardens when quenched from the temperature range 800°/950° C., than with a fully austenitic steel which does not harden appreciably when quenched from any temperature because, as will be seen later, the former steel work-hardens at a considerably faster rate than the latter.

(c) **Effect of Cold Work.** The effects of cold work on these austenitic steels have some extremely interesting features. The fact that they give very high values for elongation per cent. in tensile tests and have also a comparatively low yield point, has been adduced as evidence of great capacity for undergoing deformation when cold-worked. This is quite correct, and one of the features of the steel is its capability of being pressed, in the form of sheet, into a variety of shapes. But it should also be borne in mind that the type of tensile result obtained indicates that the material hardens considerably as a result of cold work.

As this point is rather important, occasions having arisen in which the material hardened to such an extent that the desired amount of cold work could not be performed without intermediate annealing, an operation very inconvenient as it happened in these cases, it may not be out of place to dwell on it to some extent as thereby disappointment in the use of the material for cold-working operations may be avoided. The hardening effect due to cold work and the evidence of it obtained from the tensile test may be illustrated by comparing the diagram obtained by plotting load against

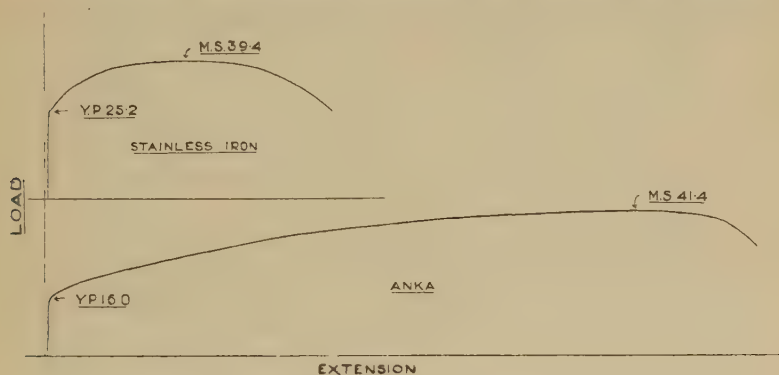


FIG. 91. Load-extension diagrams of stainless iron and "Anka" steel.

extension in a tensile test on the austenitic steel with a similar diagram obtained from stainless iron which had been hardened and tempered to give approximately the same tensile strength as the other steel. Two such curves are shown in Fig. 91. The upper curve relates to a stainless iron which gave the following results:—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on three inches.	Reduction of Area per cent.
25.2	39.4	25.0	71.7

The curve is typical of what is normally obtained from a hardened and tempered alloy steel. The yield point, occurring at 25.2 tons per square inch, is well-defined. The curve then rises to a maximum stress of 39.4 tons per square

inch. During this period of the test, the test piece is stretching and hence its cross sectional area is getting less and less. As, however, the load on the diminishing section continues to increase, the material must be hardening in order to sustain this load. Actually the cross sectional area of the test piece had decreased about 15 per cent. by the time the load had reached its maximum value. On comparing this curve with the lower curve obtained from a test piece of "Anka" steel, giving the following figures :—

Yield Point, tons per sq. inch.	Maximum Stress, tons per sq. inch.	Elongation per cent. on three inches.	Reduction of Area per cent.
16·0	41·4	60·5	71·7

the differences between the two are striking. The yield point in this case is reached at the comparatively low figure of 16·0 tons per square inch, the piece then stretching while the load continually increases. The maximum stress, 41·4 tons per square inch, is not reached until the test piece has extended 45 to 50 per cent. of its original length. At this point there was no signs of "necking" on the test piece; the latter, on the contrary, had been reduced fairly evenly in cross section.

In both cases, after the maximum load was reached, the test piece commenced to "neck," the load carried by it concurrently falling until finally it broke. During the necking process, the material at the "neck" continued, of course, to harden but during this period the rate of reduction of cross-sectional area was greater than the rate of increase in hardness of the steel; hence the actual load on the test piece diminished though the load per square inch of the reduced area continued to increase until the test piece finally broke.

The difference in behaviour of the two types of material is strikingly shown when the stress at the maximum load and at the breaking load is set out in terms of cross-sectional area at these points. Thus the figures given below indicate that, while the two materials had approximately the same tensile strength as ordinarily determined, the actual stress

intensity in the "Anka" steel was much greater than in the stainless iron.

	Stainless Iron.	"Anka."
Load in tons at maximum load ...	9.85	10.25
Stress in tons per square inch of original cross-sectional area (0.25 square inches) ...	39.4	41.4
Cross-sectional area at maximum load ...	0.212 sq. ins.	0.152 sq. ins.
Stress in tons per square inch of this area ...	46.5	66.0
Load in tons when piece broke ...	6.2	7.7
Cross-sectional area at fracture ...	0.0731 sq. ins.	0.0731 sq. ins.
Stress in tons per square inch of this area ...	85	105

A consideration of these figures would lead one to suspect that when these austenitic chromium nickel steels, such as "Anka," "V.2.A." or "Staybrite," are cold-worked, they would flow very easily at first, considerably easier, for example, than stainless iron with its higher yield point, but as the degree of cold work increases they would stiffen up much more rapidly than the stainless iron so that samples which had to be heavily cold-worked without intermediate annealing would be expected to require considerably heavier pressure or blows to perform this operation than, for example, similar pieces of stainless iron.

Actually this is found to be the case, and to give some concrete expression to this hardening effect, one may compare the behaviour of small cylinders of "Anka" steel and stainless iron when being compressed cold. Fig. 92 gives the relationship between load and reduction in height of small cylinders (0.96 in. long and 0.535 in. diameter) when compressed under steadily increasing loads and indicates that while the "Anka" cylinder lost height under small loads at a greater rate than the stainless iron, thus under a load of 10 tons the former was reduced 14.5 per cent. and the latter 7.45 per cent., the relative rates changed greatly as the load increased, so that with a load of 30 tons the

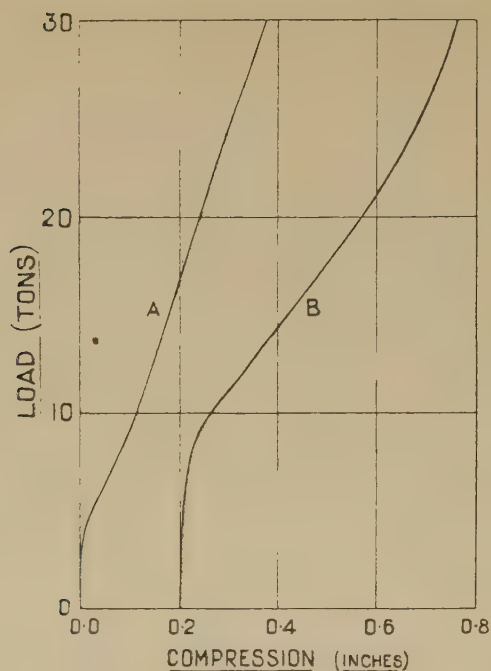


FIG. 92. Compression tests on "Anka" steel (A) and stainless iron (B).

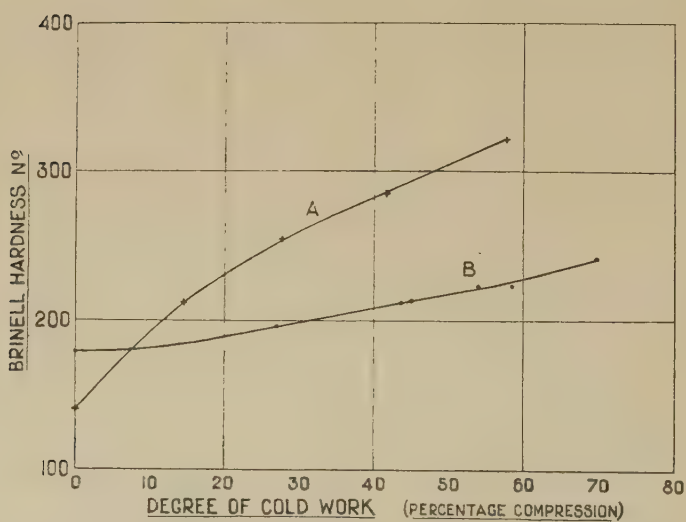


FIG. 93. Increase in Brinell hardness produced in "Anka" steel (A) and stainless iron (B) by cold-working.

"Anka" was reduced only 41.4 per cent., the corresponding figure for the stainless iron being 58.4 per cent.

Further evidence of the greater hardening of the austenitic steel, as compared with stainless iron, is shown in Fig. 93. The curves in this diagram represent the relationship between Brinell hardness and degree of cold-work in the two steels. The cold-working was produced by compressing similar small cylinders under a series of different loads, the degree of cold-work being measured by the percentage reduction in height of the cylinders when compressed.

These figures provide an explanation of what has been found in certain cases in practice. Thus experience has shown that cold rivetting operations are much more easily carried out with stainless iron than with the austenitic steels. Where rivets are being closed, those made of the latter material flow easily at first but stiffen up under the operation so that the final forming of the head is more difficult than if rivets of stainless iron are used.

In passing, it may also be noted that the capacity of the austenitic steels for hardening under cold-working accounts for the ratio between tensile strength and Brinell hardness number of these steels being greater than it is with other steels. The degree of cold-working is relatively less in the Brinell test than in the tensile test and hence the hardening effect produced in this test raises the ratio $\frac{\text{Tensile strength}}{\text{Brinell number}}$ of the austenitic steels and often to a considerable extent, as was noted earlier (page 232). Incidentally it may be observed that the value of this ratio gives an approximate idea of the workhardening capacity of the steel. The higher this ratio is, the more rapidly the material will harden by cold-work. Other things being equal therefore, a steel with as low a value as possible for this ratio should be selected for cold-working operations; if this low value is also associated with a low figure for the tensile strength of the material, so much the better.

The hardening effect produced in these austenitic steels by cold-work does not, of course, prevent them being used for cold-working operations, because the hardness so produced may easily be removed by reheating to suitable temperatures. Work-hardened samples of the steel, on being reheated to

a series of gradually increasing temperatures, behave in a similar manner to other work-hardened metals; that is, their hardness is practically unaffected by re-heating to any temperature below a certain value characteristic of the metal, though not independent of the amount of cold-work the latter has received, but re-heating to still higher temperatures produces a rapid fall in the hardness. With the austenitic chromium-nickel steels, this critical temperature occurs in the neighbourhood of 600°C .; its position, however, depends probably on the actual composition of the steel and certainly on the degree of work-hardening to which it has been submitted; with some severely cold-worked materials, softening is produced at lower temperatures than 600°C .

To give some indication of the manner in which softening (or "annealing," as it is often called in the trade) is produced, the following experiments may be quoted. Small cylinders of the steels A and B, quoted on page 229, were compressed cold. Two series of tests were carried out on each steel, the amount of compression being adjusted so that the samples were hardened to a Brinell hardness number of about 350 in one series and 280 in the other. The cylinders, which were 0.5 inches diameter and 0.75 inches long, were loaded as indicated below, the Brinell hardness numbers of the steels before and after compressing being also given:—

Steel.	Load in Tons.	Brinell Hardness Number.	
		Before Compressing.	After Compressing.
A. 	25	137	286
A. 	45	137	351
B. 	18	163	286
B. 	31	163	387

The cold-worked samples were re-heated to various temperatures (each sample being kept at the desired temperature for half-an-hour) and their Brinell hardness numbers determined after cooling therefrom. The figures showing the

relationship between hardness and re-heating temperature are plotted in Fig. 94. These curves show that a considerable amount of softening can be produced by re-heating the cold-worked material to, for example $800^{\circ}/850^{\circ}\text{C}.$, but that complete softening is only obtained at $1000^{\circ}\text{C}.$ or above.

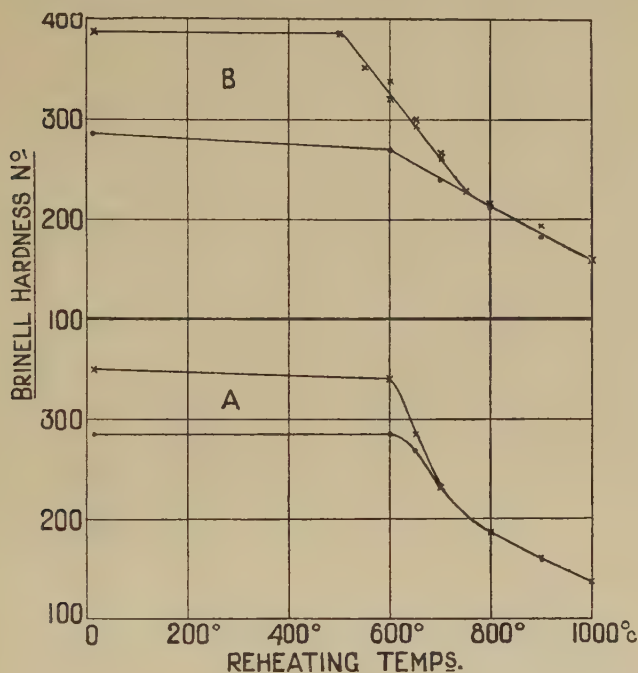


FIG. 94. Effect of reheating on the Brinell hardness of cold-worked samples of "Anka" steels.

These results have an important bearing on the commercial use of the alloys. In taking advantage of the undoubted capacity which the alloys possess of being cold-worked, it will be necessary, owing to the fact that they harden considerably when so treated, to soften them between the various stages of the operation; hence, in the manufacture of cold-pressed, cold-drawn, cold-rolled or otherwise cold-worked articles, intermediate annealings will probably be required. A reheating to a temperature of $800^{\circ}/850^{\circ}\text{C}.$ produces only a thin coloration on the surface of a previously bright article made of these alloys and if, as is probably the case, the amount of softening produced by such a treatment

is ample for most purposes, there would be no necessity to use the method of "close annealing" for these intermediate annealings and probably pickling would be unnecessary except before the final stage in the cold-working operations. The use of a temperature of 1000°C. or over so as to give completely softened material would result in a considerably greater liability for scaling in the articles.

It may not be out of place here to point out the necessity, for such cold-working operations, of using a steel which is completely austenitic. It was shown in Chapter IV (pages 126-132) that a certain minimum amount of nickel was required in a steel of given chromium content in order that the resulting alloy should be austenitic after reheating to any temperature, or in other words, in order that it should not harden by quenching from any temperature. If rather less than this requisite amount of nickel is present, the resulting alloy is quite soft after quenching from high temperatures, e.g., 1000°C. or over, but hardens considerably after reheating to and cooling from temperatures in the range 750° to 950°C. An example of such an alloy, containing 13.7 per cent. chromium and 7.85 per cent. nickel, was given on page 128, its capacity for hardening after heating in the temperature range mentioned being indicated in Fig. 68. Nickel being an expensive constituent of steel, it would not be surprising if attempts were made in the interests of economy to cut down the nickel content of these alloys to as low a figure as possible. If the material is to be used for articles which are hot forged or rolled to shape, requiring only a subsequent machining, and which in the course of their use are not likely to be heated in the range 750° -' 950°C. , such an alloy as that mentioned above may be perfectly satisfactory because a single reheating to a temperature of about 1050°C. , after the forging or rolling operation, will put the material in a satisfactory condition. If, however, the material has to be cold-worked, its limitations become apparent. As a result of such treatment, it hardens of course in the same way as the higher nickel alloys, but at a faster rate so that relatively less work may be put on it than the higher nickel alloy before it requires softening. On reheating the hardened material, it behaves in a similar manner to the hardened form of the same alloy which is produced by reheating in the range 750° /' 950°C. ; that is, it softens very slightly after reheating

in the neighbourhood of $600^{\circ}\text{C}.$, but on reheating to higher temperatures it re-hardens again in the manner illustrated in curve B, Fig. 68. To give some quantitative expression to this behaviour, it may be mentioned that cylinders, half-an-inch diameter and three-quarters of an inch long, of the steel described above, containing 13.7 per cent. chromium and 7.85 per cent. nickel, were compressed cold, causing a reduction in their length of 24 per cent. Before compressing, they had been quenched in water from a temperature of $1050^{\circ}\text{C}.$ and had a Brinell hardness number of 196; after compressing, this value had increased to 364, a figure of the same order as that obtained from the fully austenitic steels only by the much greater cold-working involved in reducing similar sized cylinders some 60 or 70 per cent. of their length as is indicated in Fig. 93. On reheating the hardened samples to a series of gradually increasing

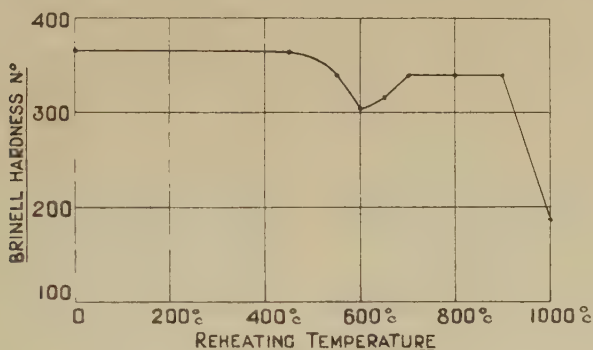


FIG. 95. Effect of reheating on the Brinell hardness of cold-worked samples of chromium-nickel steel which is not fully austenitic (see page 240).

temperatures, the results plotted in Fig. 95 were obtained; a comparison of this curve with curve B in Fig. 68 shows the striking similarity between the two. From the point of view of the producer of cold-worked articles, however, the difference in behaviour between this material and the fully austenitic alloy as evidenced by a comparison of Figs. 94 and 95 is most important. In the one case, softening is produced at temperatures exceeding about $600^{\circ}\text{C}.$, in the other a minimum of $1000^{\circ}\text{C}.$ is required. The moral of these results is obvious; material such as that used for the tests in Fig. 95 hardens up very rapidly on being cold-worked

and can only be softened by reheating to a temperature of 1000°C. or over. It is therefore a decided advantage for the user of these austenitic alloys who wishes to cold-roll, cold-press, cold-draw, or otherwise cold-work them, to make certain that he obtains material which is fully austenitic, i.e., does not harden when reheated to and cooled from the range $750^{\circ}/950^{\circ}\text{C.}$

It is interesting to note that the austenitic alloys, which are, of course, non-magnetic in that condition, become distinctly magnetic after they have been cold-worked. The magnetic effect is especially marked with the "borderland" alloys, such as that illustrated in Fig. 95, which are not fully austenitic. The presence of magnetism in the cold-worked material is interesting theoretically, as it indicates a change of phase as a result of cold-work, the non-magnetic γ iron changing in part, at least, to the magnetic α form. Such a magnetic effect has been noted with other austenitic alloys.*

(d) **Microstructure.** Compared with stainless steel or iron, the structure of these austenitic chromium-nickel alloys is relatively simple. After quenching or air-cooling from $1000^{\circ}/1100^{\circ}\text{C.}$, they consist of grains of austenite; some free carbide, to an amount depending on the carbon content of the alloy, may also be present. The characteristic structure of such austenite is seen in Fig. 96. This photograph, taken from an alloy containing only 0.10 per cent. carbon, does not show any free carbide. In hot-worked samples the austenite grains are more or less distorted, to an extent depending on the temperature at which the forging or rolling was carried out; they are also frequently crossed by series of fine parallel lines as shown in Fig. 97.

Under the influence of cold-work, the grain distortion becomes more pronounced; in addition, the series of fine lines become much more numerous producing, with severe distortion, a very dark appearance in parts of the grains in the manner indicated in Fig. 98. On reheating to 1000°C. , both the grain distortion and the line effect are removed

* Definite confirmation of this change of phase due to cold-work has quite recently been published by Dr. Hatfield (Metallurgical Supplement, *Engineer*, October 30th, 1925). Samples of "Staybrite" steel, before and after cold-working, were sent to Dr. Westgren (of Stockholm) for X-ray examination of their crystal structure. Dr. Westgren's X-ray photograms show conclusively that the original face-centred lattice structure of the γ -iron (austenite) in the soft material had been changed in part by cold working into the body-centred lattice, characteristic of α -iron



FIG. 96. "Anka" steel, 0.10 % carbon, 15.2 % chromium and 11.4 % nickel, fully softened. $\times 300$.



FIG. 97. "Anka" steel, 0.10 % carbon, 15.2 % chromium and 11.4 % nickel, as rolled. $\times 750$.



FIG. 98. "Anka" steel, 0.10 % carbon, 15.2 % chromium and 11.4 % nickel, cold-worked to a Brinell hardness number of 350. $\times 750$.

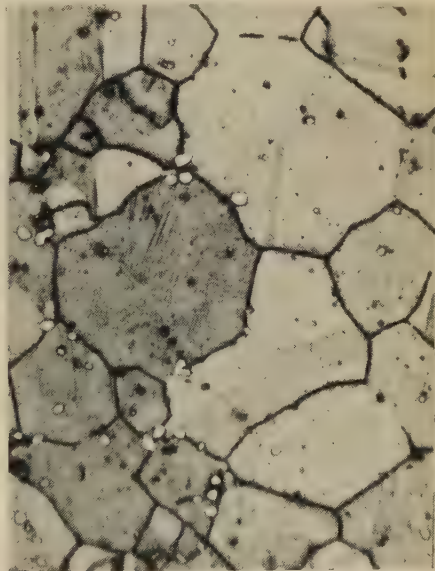


FIG. 99. Free carbide in a high carbon austenitic alloy containing 0.44 % carbon, 20.0 % chromium and 6.47 % nickel, fully softened. $\times 300$.

[To face page 242.

during the recrystallisation which then takes place. Free carbide occurring along with austenite in a higher carbon alloy is illustrated in Fig. 99.

(e) **Tests at High Temperatures.** It has been mentioned that these alloys are somewhat harder to roll or forge than ordinary stainless steel. This behaviour is reflected in the results obtained from tensile tests at high temperatures on the different steels. Under similar conditions of testing, samples of the "Anka" alloy had a tensile strength at 700° C., four to five tons per square inch higher than that obtained from a stainless steel containing 0.35 per cent. carbon and 11.2 per cent. chromium; at 800° C., the difference had fallen to rather less than three tons per square inch.

(f) **Scaling Tests.** The relative resistance to oxidation at high temperatures of mild carbon steel, stainless steel and the austenitic alloy is shown by the following tests. Cylinders of the steels ($1\frac{1}{4}$ " diameter, 1" long) were heated together in a gas furnace for the following periods:—

A.	4½ hours.	900°/950° C.
B.	18 "	975°/1025° C.
C.	5 "	1050°/1150° C.

At the end of each period, the samples were removed from the furnace, the scale detached as completely as possible and loss of weight determined. The results are given in the following table, the losses being returned both as grams per square cm. per hour and as a percentage of the original weight.

Material.	PERIOD A. 4½ hrs. at 900/950° C.		PERIOD B. 18 hrs. at 975/1,025° C.		PERIOD C. 5 hrs. at 1,050°/1,150° C.	
	Loss in grms. per sq. cm. per hour.	% Loss.	Loss in grms. per sq. cm. per hour.	% Loss.	Loss in grms. per sq. cm. per hour.	% Loss.
Mild Steel ...	0.027	3.51	0.033	16.1	0.115	14.0
Stainless Steel ...	0.0088	1.21	0.012	6.4	0.064	9.3
"Anka" Alloy ...	0.00125	0.15	0.0057	2.8	0.032	4.4

The total loss in weight of the three steels, expressed as a percentage of their original weights, after the three periods in the furnace were 33.6, 16.9 and 7.3 per cent. respectively.

In a further test, three somewhat larger samples ($1\frac{1}{2}$ " long, 1" diameter) were heated in a gas-fired furnace for three days at 1,000° C. ($\pm 25^\circ$ C.). The losses in this case after removal of the scale were :—

Material.						Loss, per cent. of Original Weight.
Mild Steel	45.1
Stainless	17.9
"Anka"	5.1

These results show that the nickel chromium alloy resists scaling very well up to about 950° C. but scales more heavily at higher temperatures. Even at the highest temperature tried, however, it scaled at a considerably slower rate than either mild steel or ordinary stainless steel.

(g) **Resistance to Corrosion.** Compared with ordinary stainless steel containing 12 to 14 per cent. chromium, the austenitic nickel-chromium alloys have a distinctly greater resistance to certain types of corrosion, due partly to their greater chromium content and partly to the large amount of nickel they contain; it is also possible that the fact that they are austenitic alloys may have some bearing on their corrosion resisting qualities. Some of these beneficial effects may be summarised as follows :—

(i) The resistance of the austenitic steel to the attack of some mineral acids, notably sulphuric and hydrochloric, is considerably greater than that of ordinary stainless steel. The austenitic alloy certainly cannot be regarded in some cases as an "acid-resisting steel" but its rate of attack is only a small fraction of that of stainless steel under similar conditions. It seems probable that the increased resistance

to sulphuric and hydrochloric acids is largely due to the high nickel content of the alloy.

(ii) In common with steels containing the same amount of chromium but free from nickel, the nickel-chromium alloy is quite unattacked by nitric acid of any strength either at ordinary temperatures or at 80°/85° C.

(iii) Certain organic acids, such as citric, oxalic, formic, and tartaric, which have a distinct action on stainless steel, have either no action at all, or only a very slight attack on the austenitic alloy.

(iv) Under certain conditions, ordinary stainless steel is liable to suffer electro-chemical attack when in contact with copper or some of its alloys or graphite when both are immersed in certain electrolytes. This does not appear to take place with the nickel-chromium alloys.

(v) The resistance to general corrosion of the austenitic material is at least as great as that of the lowest carbon stainless steel containing the upper limit of chromium content and in the most resistant form produced by heat treatment.

(vi) The resistance to general corrosion of the austenitic alloy appears to be less affected by cold-work than does that of ordinary stainless steel.

(vii) The austenitic alloy is resistant to some of the aqueous solutions of salts which attack ordinary stainless steel; for example, solutions of all strengths of ammonium sulphate, alum, potassium sulphate and sodium sulphate have no action on it.

The increased resistance to acids is indicated by the results given in Table XXIX. In the experiments to which these refer, polished samples of—

(i) The austenitic alloy, "Anka" brand, containing 15.2 per cent. chromium and 11.4 per cent. nickel.

(ii) A similar alloy but of the "V.2.A." type, containing 20.4 per cent. chromium and 8.6 per cent. nickel.

(iii) A typical stainless steel, containing 0.3 per cent. carbon and 12.2 per cent. chromium, which had previously been hardened at 900° C. followed by tempering at 700° C. and

(iv) An ordinary mild steel containing 0.35 per cent. carbon, 0.23 per cent. silicon, and 0.71 per cent. manganese were exposed to the various acid media for the periods

TABLE XXIX.

Rate of Attack of Acids on "Anka" "V.2.A." Stainless and Ordinary Mild Steels.

Acid.	Strength.	Temperature.	Duration of Attack.	Loss in mgm. per sq. cm. per hour.			
				"Anka."	V.2.A.	Stainless.	Mild Steel.
Hydrochloric	10%(N)	18/20°C	48 hrs.	0.038	0.07	1.15	2.34
"	50%(5N)	"	48 "	0.25	0.36	3.25	5.9
Sulphuric	5%	"	48 "	0.065	0.087	2.7	4.2
"	35%	"	24 "	0.155	0.304	8.9*	6.7*
"	50%	"	48 "	0.35	0.39	0.16	0.08
"	10%	60/65°C	6 "	4.6	4.2	—	93.5
"	20%	"	6 "	10.3	11.9	—	122
"	30%	"	6 "	17.6	17.7	—	—
Nitric	Normal	18/20°C	6 "	nil.	—	1.46	22.1
"	"	80/85°C	6 "	nil.	—	1.09	85
"	5N	"	6 "	nil.	—	0.025	—
Phosphoric	5%	18/20°C	24 "	nil.	—	0.05	1.10
"	"	"	8 days	nil.	—	—	—
"	25%	"	24 hrs.	nil.	—	0.20	2.60
"	"	"	8 days	nil.	—	—	—
"	66%	"	48 hrs.	0.052	0.113	0.47	4.62
	(S.G. 1.5)						
Acetic	5%	18/20°C	14 days	nil.	—	0.014	0.067
"	"	80/85°C	30 hrs.	nil.	—	—	—
"	15%	18/20°C	14 days	nil.	—	0.012	0.105
"	"	80/85°C	30 hrs.	nil.	—	—	—
"	33%	18/20°C	14 days	nil.	—	0.012	0.115
	(B.P.)						
"	"	80/85°C	30 hrs.	nil.	—	—	—
"	Glacial	18/20°C	14 days	nil.	—	nil.	0.124
"	"	80/85°C	27 hrs.	nil.	—	0.015	0.89
Citric	6%	18/20°C	14 days	nil.	—	0.011	0.260
Formic	10%	18/20°C	12 "	0.011	0.014	0.26	0.33
Oxalic	6.3%(N)	"	7 "	0.013	—	0.021	0.036
Tartaric	7.5%(N)	"	14 "	nil.	—	0.0085	0.062
"	25%	"	14 "	nil.	—	0.045	0.270

* These figures are probably low, due to the gradual retardation of attack produced by the using up of the acid and the accumulation of sulphates in the solutions.

indicated. The losses are given in milligrams per square centimetre per hour. The results with hydrochloric and sulphuric acids indicate that the austenitic alloys are reasonably resistant to dilute solutions of these acids at atmospheric temperatures. On heating the acids, however, the rate of attack increases rather rapidly.

Further data on the resistance of these alloys to various reagents were given by Dr. Hatfield in an article entitled "The Possibilities of Stainless and Similar Corrosion-Resisting Steels in the Chemical and Allied Industries."* The results given therein were obtained with the "Staybrite" type of alloy (containing 18 per cent. chromium and 8 per cent. nickel) but they apply equally well to the "V.2.A." and "Anka" types. The original publication by Drs. Strauss and Maurer on these alloys (see page 227) also contains data on their corrosion-resisting properties.

(h) Physical Properties.†

(1) *Moduli of Elasticity.* The following data, obtained from the "Anka" type of the steel, indicate that the austenitic material has slightly lower values of the moduli of elasticity than ordinary stainless steel (see pp. 101 and 103):—

	lbs. per sq. in.
Modulus in Tension (Young's Modulus)...	28.6×10^6
„ „ Shear	11.9×10^6

(2) *Density.* This varies to some extent with composition owing to chromium having a lower, and nickel a higher, density than iron. The "Anka" type of the steel, having the higher nickel and lower chromium content is somewhat heavier than the "V.2.A." type, "Staybrite" occupying an intermediate position. The presence of appreciable amounts of silicon in an alloy makes its density lower than it otherwise would be. The density of any one sample of the steel is also affected to a small extent by the treatment it has received, cold work tending to lower the value. The following are some typical figures:—

* *The Industrial Chemist.* March, 1925. p. 64.

† All the values for "Staybrite" given in this section are taken from Dr. Hadfield's article "Chromium Nickel Rustless Steel," *Engineer*, Metallurgical Supplement, October 30th, 1925.

Type.	Chromium. %	Nickel. %	Silicon. %	Treatment.	Density.
"Anka" ...	15.2	11.4	0.25	Fully softened.	7.971
" " ...	"	"	"	Cold worked to a Brinell num- ber of 300/350.	7.942
" " ...	15.0	9.0	1.34	Fully softened.	7.879
"V.2.A." ...	20.5	6.64	0.31	ditto.	7.870
" " ...	20.2	8.4	0.26	ditto.	7.883
"Staybrite" ...	18	8	—	—	7.86-7.925

(3) *Electrical Resistance.* This again is affected to some extent by variations in composition, as would be expected. The following values may be quoted :—

Type.	Chromium. %	Nickel. %	Silicon. %	Specific Resistance.
"Anka" ...	15.2	11.4	0.25	0.0000740 ohms. per cm. ³
" " ...	15.0	9.0	1.34	0.0000828 " " "
"Staybrite" ...	18	8	—	0.000069 " " "

(4) *Co-efficient of Expansion.* The austenitic alloys have a considerably greater co-efficient of expansion than ordinary stainless steel, a point which should be borne in mind in the engineering application of the material. The values given in Table XXX are typical, and may be compared with those given on page 143 for ordinary stainless steel.

(j) *Welding, Brazing and Soldering.* The austenitic alloys may be soldered or brazed without difficulty. They may also be welded with the electric arc or the oxy-acetylene blowpipe more easily than ordinary stainless material. As they do not harden on cooling rapidly from high temperatures, they do not suffer from the disabilities of ordinary stainless steel in this respect. They may also be welded by the above processes to ordinary stainless steel, giving very satisfactory joints.

TABLE XXX.

*Co-efficient of Expansion of "Anka" and
"Staybrite" Steels.*

Type.	Chromium. %	Nickel. %	Temperature Range.	Mean Co-efficient of Expansion per ° C.
"Anka" ...	15.4	10.3	20°-200°C.	0.0000180
			200°-400°C.	0.0000187
			400°-600°C.	0.0000195
			600°-800°C.	0.0000203
			20°-400°C.	0.0000184
"Staybrite" ...	18	8	20°-600°C.	0.0000186
			20°-800°C.	0.0000191
			20°-100°C.	0.000017
			20°-200°C.	0.0000177
			20°-300°C.	0.0000181
			20°-400°C.	0.0000186
			20°-500°C.	0.0000192
			20°-600°C.	0.0000201

C. CHROMIUM-NICKEL-SILICON STEELS. By increasing the nickel content to about 25 per cent., the chromium remaining in the range 15 to 20 per cent. and also adding two to three per cent. silicon, still greater resistance is obtained to the attack of acids at ordinary temperatures and to scaling at high temperatures. In these respects such alloys compare very favourably with the alloys of the "nichrome" type containing 60 per cent. or so of nickel and at the same time are much cheaper than the latter.

The degree of resistance of this type of steel, the properties of which were first described by C. M. Johnson,* to some acids is shown in Table XXXI, in which the properties of such an alloy are compared with those of an alloy of the "nichrome" type, which is acknowledged to possess very good resistance to acids. These tests were carried out at atmospheric temperature, the duration of each test being 48 hours. The losses, as in previous tables, are given in milligrams per square centimetre of surface per hour and as a percentage of the original weight of the sample, these

* *Trans. Amer. Soc. for Steel Treating.* I. 554 (1921).

having each a weight of about 25 grams and a surface area of about 12·5 square centimetres.

TABLE XXXI.

Resistance of Nickel Chromium Alloys to Acid Attack at Atmospheric Temperature.

Alloy.	Carbon %	Silicon %	Chromium %	Nickel %
A 	0·34	2·35	17·7	25·8
B 	0·41	0·50	11·1	64·3

Acid.	Strength.	Loss, mgm. per sq. cm. per hour.		Loss in per cent. of original weight.	
		A.	B.	A.	B.
Sulphuric ...	5%	0·015	0·012	0·038	0·028
„ ...	35%	0·012	0·011	0·030	0·026
„ ...	50%	0·02	0·008	0·048	0·019
Hydrochloric ...	10%	0·021	0·016	0·053	0·038
„ ...	Normal.				
„ ...	50% (5N)	0·22	0·15	0·54	0·36
Nitric ...	Normal	0·04	1·70	0·10	4·16
Acetic ...	5%	nil.	0·011	nil.	0·027

It will be seen that at atmospheric temperatures, the 25 per cent. nickel alloy gives really better all-round results than the higher nickel alloy because, although the latter is very slightly the better in its resistance to sulphuric and hydrochloric acids, the former is not attacked at all by the dilute acetic acid and is much superior in its resistance to dilute nitric acid, which has a really extraordinary attack on the high nickel alloy.

The action of dilute nitric acid on both these alloys is interesting in that it indicates that chromium is the addition giving immunity from the attack of this acid. A steel containing 17·7 per cent chromium but free from nickel would be entirely unaffected by dilute nitric acid although alloy A in Table was slightly attacked. Similarly an

ordinary stainless steel containing carbon and chromium as in alloy B but free from nickel would not have lost anything like 4 per cent. of its weight after a 48 hours' attack with normal nitric acid.

At temperatures above atmospheric, however, the lower nickel alloy shows to much less advantage. The rate of attack of sulphuric acid on this alloy increases rather rapidly as the temperature rises above atmospheric so that if comparisons are made at such higher temperatures the advantage is very much in favour of the "nichrome" type of alloy. For example the results obtained by the attack of acids at 60°-65° C. are given in Table XXXII, and they indicate the marked superiority of the higher nickel alloy. The results with hydrochloric acid indicate that neither alloy is particularly resistant to hot solutions of this acid, especially when fairly strong. The action of hot dilute nitric acid is also interesting and confirms what was said earlier as to the action of nickel and chromium with respect to this acid.

TABLE XXXII

*Resistance of Nickel Chromium Alloys to Acid Attack
at 60°-65° C.*

Alloy.	Carbon %	Silicon %	Chromium %	Nickel %
A	0.34	2.35	17.7	25.8
B	0.41	0.50	11.1	64.8

Acid.	Strength.	Loss, mgm. per sq. cm. per hour.		Per cent. loss in 6/6½ hours.	
		A.	B.	A.	B.
Sulphuric	10%	1.67	0.127	0.54	0.038
"	20%	4.57	0.108	1.48	0.033
"	30%	6.85	0.105	2.21	0.032
Hydrochloric	10% (N)	0.93	0.81	0.28	0.24
"	50% (5N)	14.7	9.6	4.49	2.84
Nitric	Normal.	2.01	18.8	0.60	5.55

With regard to resistance to oxidation at high temperatures, samples $1\frac{1}{2}$ in. long, 1 in. diameter and weighing about 150 grams of the two alloys mentioned above were exposed (along with the mild steel, stainless steel and "Anka" samples described on page 244) in a gas-fired furnace for three days at $1000^{\circ}\text{C.} (\pm 25^{\circ}\text{C.})$. After this treatment both were covered with a thin adherent film and showed a total gain in weight of less than 0.10 per cent., a result which may be compared with the figures for the other steels given on page 244. These two samples were then put back in the furnace for a further period of seventeen days, the temperature range being as before. During this period the furnace containing the samples was allowed to cool down during the week-ends: this time, however, is not counted in the number of days given above. At the end of the test, the samples were covered with a thin adherent scale. After removing this scale, the alloy with 25 per cent. nickel and 17 per cent. chromium was found to have lost 0.18 per cent. of its weight while the "nichrome" alloy had lost 0.05 per cent. Both samples were then put back in the furnace and the temperature of the latter maintained at 1100°C. for four and a quarter days. After this treatment, the "nichrome" alloy had lost 0.4 per cent. of its weight and the other alloy 0.9 per cent. In all these tests, an oxidising atmosphere was maintained in the furnace the whole time. The results indicate that the alloy with 25 per cent. nickel and 17 per cent. chromium is remarkably resistant to oxidation.

It was shown by Kayser* that nickel-chromium alloys of the "nichrome" type, though possessing an extraordinary resistance to oxidation at high temperatures, were readily attacked, if exposed at these temperatures to gases containing sulphur dioxide or sulphuretted hydrogen. The alloy with 25 per cent. nickel and 17 per cent. chromium appears to have the same disability.

In addition to resisting oxidation at high temperatures, this alloy is also much stronger at a red heat than either stainless steel, or the lower nickel alloys such as "Anka." Tensile tests carried out in a manner comparable with those detailed earlier in the book give for this alloy a tensile strength of about 40 tons per square inch at 600°C. , 29 tons

* Heat and Acid-Resisting Alloys (Ni-Cr-Fe). J. F. Kayser, *Trans. Faraday Soc.*, XIX, p. 184.

per square inch at 700° C., 22 tons per square inch at 800° C., and 16 tons per square inch at 900° C.

Such high nickel-chromium alloys as these are austenitic in character ; they cannot be hardened by quenching though they may be, of course, by cold-work. Their mechanical properties may be indicated by the following tests obtained from bars one-inch diameter of material containing 0·34 per cent. carbon, 2·35 per cent. silicon, 17·7 per cent. chromium, and 25·8 per cent. nickel.

Treatment.	Yield Point, tons per sq. inch.	Max. Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hard- ness Number.	Izod Impact, ft. lbs.
As Rolled ...	26·0	50·5	23·5	41·9	223	35, 35, 35.
W.Q. 1,000° C....	18·0	46·6	36·0	49·7	179	54, 55, 65.

As with other austenitic steels, quenching in water from about 1000° C. is a suitable softening treatment.

Soldering, brazing and welding may be carried out without difficulty on these chromium-nickel-silicon steels; in fact these operations are even more readily performed with this type of material than they are with the chromium-nickel steels described in the last section.

One of the uses to which the nickel-chromium alloy containing 25 per cent. nickel has been put is for the manufacture of valves for internal combustion engines where extremely severe conditions are encountered. Valves made of this material, owing to their strength at high temperatures and their great resistance to oxidation, have been found very valuable. It should be remembered in this respect, however, that this alloy, like the "Anka" type, has a much larger co-efficient of expansion than stainless steel. Thus the following figures were obtained from the alloy, the mechanical tests of which are given above.

Temperature Range.	Co-efficient of expansion.
15 - 400°	0·0000175
400 - 600°	0·0000183
600 - 800°	0·0000193

This higher co-efficient of expansion should be borne in mind and sufficient clearance allowed between valve stem

and guides, otherwise the greater expansion of the valve on heating may cause it to bind.

The density of this type of alloy is lower than would be expected from its high nickel content; thus a sample of the material used for the various tests which have been quoted on the preceding pages and containing 0.34 per cent. carbon, 2.35 per cent. silicon, 17.7 per cent. chromium and 25.8 per cent. nickel had a density when fully softened of 7.836. The fact that the density is so low is attributable to the high silicon content.

D. CHROMIUM-MOLYBDENUM STEELS. The resistance of chromium-molybdenum-iron alloys to chemical attack, more particularly of acids, was noted by Borchers and Monnartz some years ago. In 1910 they took out a German Patent (No. 246,035) in respect of alloys containing 10 to 60 per cent. chromium, together with 2 to 5 per cent. molybdenum, claiming for them high resistance to chemical action and mechanical workability. They also claimed that the molybdenum could be partly replaced by vanadium or titanium.

By the addition of about 2 per cent. molybdenum to an ordinary stainless steel, the resistance of the latter to both mineral and organic acids is decidedly increased. As an indication of this, the results given in Table XXXIII and obtained on two stainless steels similar in analysis except that one contained just over 2 per cent. molybdenum, may be quoted. Both the steels were in the hardened and tempered condition. The tests were carried out at atmospheric temperature.

With regard to the effect of such a content of molybdenum on the mechanical properties of the steel, experiments indicate that the presence of this metal

- (a) raises the temperature of the Ac.1 point,
- (b) reduces to a distinct extent the air-hardening capacity of the steel, at any rate, when cooled from the range of temperature of about one hundred degrees or so above the Ac.1 point.

These effects are apparent from the curves in Fig. 100. Curves A and B indicate the Brinell hardness numbers obtained from a steel containing 0.24 per cent. carbon,

12·8 per cent. chromium, and 2·24 per cent. molybdenum. The figures plotted in curve A refer to small discs water quenched from the temperatures indicated while those in B were obtained from bars, one inch diameter, which had been air-cooled. For comparison, curve C represents typical figures obtainable on air or oil hardening a steel free from molybdenum but otherwise of similar composition.

TABLE XXXIII.

*Effect of Molybdenum on the Acid Resistance of
Stainless Steel.*

			Carbon %	Chromium %	Molybdenum %	
Steel A	0·32	12·2	nil.	
Steel B	0·23	11·6	2·3	

Acid.	Strength.	Duration of Test.	Loss %		Loss in mgm. per sq. cm. per hour.		
			A.	B.	A.	B.	
Nitric	...	Normal	6 hrs.	0·54	0·206	1·76	0·67
Hydrochloric	10%	24	„	2·59	0·24	2·15	0·20
Sulphuric	...	5%	24	„	4·90	1·65	4·09
„	...	35%	6	„	3·16	0·525	20·5
Acetic	...	5%	8 days	0·785	0·045	0·079	0·0045
„	...	33%	10	„	1·15	0·109	0·093
Citric	...	6%	7	„	2·08	0·071	0·24
Tartaric	...	25%	13	„	0·68	0·34	0·043

Presuming, however, that a suitable hardening temperature is used for the molybdenum steel, the latter, when subsequently tempered, behaves very similarly to an ordinary stainless steel. Probably the molybdenum steel is somewhat harder when fully-tempered than a steel free from this metal, but otherwise the presence of the molybdenum would appear to have little effect on the properties of the steel. Thus a bar one inch in diameter of the steel referred to above, containing 2·24 per cent. molybdenum, 0·24 per cent. carbon, and

12·8 per cent. chromium, when oil-quenched from 950° C., and then tempered at 700° C., gave the following tests :—

Yield Point, tons per sq. inch.	Max. Stress, tons per sq. inch.	Elonga- tion per cent. on 2 ins.	Reduc- tion of Area per cent.	Brinell Hardness No.		Izod Impact, ft. lbs.
				After Hardening.	After Tempering.	
34·0	49·6	27·0	59·3	332	235	47, 55, 46.

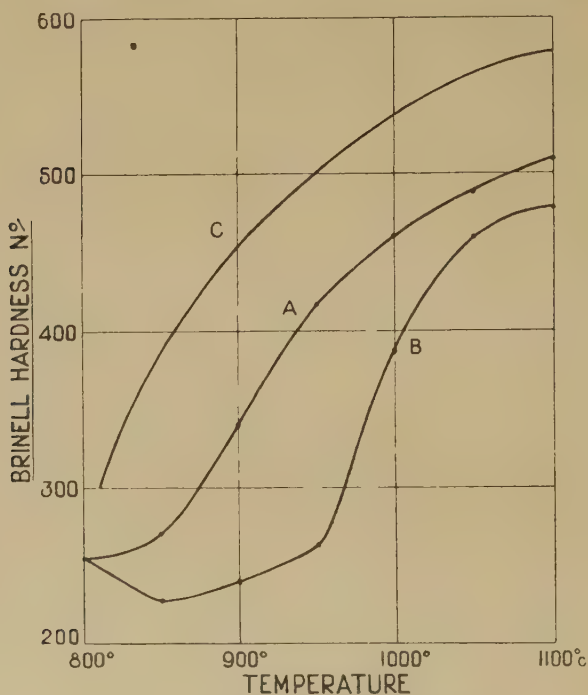


FIG. 100. Brinell hardness numbers obtained from chromium-molybdenum steel containing 0·24 % carbon, 12·8 % chromium, 2·28% molybdenum after water quenching (Curve A) or air cooling (Curve B) from the temperatures indicated. Curve C gives typical results obtainable on air cooling a steel free from molybdenum, but otherwise similar in analysis.

The yield point is somewhat low, an effect which may be attributed to the fact, indicated by the Brinell hardness number, that the steel was not fully hardened by oil-quenching from 950° C. The maximum stress is also rather higher than would be obtained from an ordinary stainless steel of the

same carbon content after similarly hardening and tempering (compare with results in Table III, p. 85), but apart from this the results are typical of ordinary stainless steel.

E. COMPLEX ALLOYS. The addition of other metals, among them copper, molybdenum and tungsten, to both types of the nickel-chromium alloys described earlier in this chapter has been suggested for the purpose of improving the qualities of these alloys in certain directions, such, for example, as increased resistance to acids or other special forms of corrosion or to oxidation at high temperatures, and greater strength at such temperatures.

With regard to acid resistance, Krupps have patented* a series of alloys having the following range of composition :

Carbon	0.1 to 0.4 per cent.
Chromium	18 to 30 per cent.
Nickel	20 to 4 per cent.
Molybdenum	2 to 4 per cent.

for which special resistance to sulphurous acid at high temperatures is claimed, a suggested use being in the manufacture of cellulose. It will be noted that the alloy may be regarded as a modification of their V.2.A. type brought about by the addition of molybdenum. Such an alloy containing molybdenum possesses also a very marked resistance to very dilute sulphuric acid ; with strong solutions of this acid, the molybdenum appears to increase the rate of attack. The effect of the added molybdenum may be gauged from the results given in Table XXXIV, obtained on an alloy of the V.2.A. type and one of similar composition but containing 3.8 per cent. molybdenum.

A further modification of the V.2.A. type has also been patented by Krupps,† the added metal in this case being copper (2 to 6 per cent). This special alloy is claimed to have exceptional resistance to the attack of ammonium chloride solutions.

Various other proprietary alloys of a more or less complex nature are on the market, e.g., the S.A. de Commentry Fourchambault et Decaseville have protected an alloy,

* British Patent No. 201,915 (July, 1923).

† British Patent No. 201,914 (July, 1923).

TABLE XXXIV.

Effect of Molybdenum on the Resistance to Sulphuric Acid of Chromium-Nickel Steels.

	Carbon %	Chromium %	Nickel %	Molybdenum %
Alloy A	0.34	20.4	8.6	nil.
Alloy B	0.44	20.5	6.5	3.8

Strength of Acid.	Temperature.	Duration of Attack.	Loss in mgm. per sq. cm. per hour.	
			Alloy A	Alloy B
5%	18° C.	48 hours.	0.087	nil*
10%	"	"	0.098	nil*
15%	"	"	0.13	0.09
20%	"	"	0.13	0.14
25%	"	"	0.20	0.27
35%	"	"	0.30	0.71
50%	"	"	0.39	0.61
10%	60/65° C.	6 hours.	4.2	nil†
20%	"	"	11.9	15.8
30%	"	"	17.7	29.7

"A.T.V.", for which stability and strength at high temperatures as well as resistance to corrosion are claimed. The author understands that this is a chromium-nickel alloy containing 10 or 15 per cent. of the former and 25 to 40 per cent. of the latter, together with smaller amounts of molybdenum, tungsten and vanadium, and also that the manufacturing rights for this country are held by Messrs. Hadfields, Ltd. A complex iron-silicon-chromium-tungsten alloy, which may also contain nickel, manganese, copper, cobalt, vanadium, titanium, and aluminium, has also been patented by Sir R. A. Hadfield‡ for which superior resistance

* No attack in five months.

† No attack after two days; temperature then raised to 80°/85°C., no action after 30 hours

‡ British Patent No. 220,006 (Feb. 9th, 1923).

to corrosion at both atmospheric and high temperatures is claimed. There are also other types. Little, however, has been published with regard to the properties of such complex alloys, which would enable one to compare them with the simpler chromium-nickel alloys and thus to judge the effect of the extra alloying metals. Probably, however, there is a fruitful field for research in investigating the properties of these and other complex alloys more particularly from the point of view of providing materials to withstand exceptionally severe conditions of attack, especially at temperatures above atmospheric, such as are met with in the chemical industry.

SOME APPLICATIONS OF STAINLESS STEEL

CHAPTER VIII

SOME APPLICATIONS OF STAINLESS STEEL

It has already been mentioned that very little opportunity occurred for developing the use of stainless steel for various engineering purposes until after the end of the war. Certainly, experience had been gained during the war period in certain directions partly as a result of experimental work by a few engineers and others who were enthusiastic about the virtues of the new material. Such experimental work, however, was more or less of an isolated character; it cannot be said that any general engineering use had been made of stainless steel up to the end of 1919. Since that time considerable progress in the use of the steel has been made in several directions while its possibilities have been indicated in others. In this chapter it is not proposed to give a long list of the many purposes for which it has been suggested that the steel should be used but, rather, to give a brief account of the results of its application for certain engineering purposes; it is thought that such a description will be the more interesting and illuminative to engineers. In addition, an attempt has been made to analyse some of the physical properties required in material for some of these purposes; it is hoped that this analysis, and also the suggestions as to which particular types of stainless material would appear to be most suitable under different manufacturing or service conditions will be of assistance to those who may wish to use some type of rust-resisting steel but who do not quite realise the range of material available or the necessity which exists for discriminating between one grade of the steel and another.

It is not proposed to dwell on the use of the material for cutlery purposes. Mention has already been made of the fact that stainless steel was first used commercially for knife making, while in the last chapter some consideration was given to the characteristics required from a knife in relation to the chromium content of the steel.

From its initial use for table cutlery, obvious steps have led to its adoption for other classes of knives, such as pocket knives, or those of a more or less technical application such as butchers' knives and also for scissors and for surgical instruments. Types of the last named which require no cutting edge should be made from steel having a distinctly lower carbon content than that used for knives and other articles used for cutting purposes; probably about 0.15 per cent. is suitable. In passing it may be mentioned that "Lysol" and other similar disinfectants have no action on stainless steel so that instruments made of this material may be sterilised with such fluids without being damaged in any way. Corrosive sublimate (mercuric chloride), however, is not a suitable disinfecting medium for such instruments. The very dilute solution of this salt used for such purposes, containing 0.1 per cent. of the salt, has certainly only a very slight action on stainless steel; such action as would be likely to take place, however, would probably lead to the formation of very minute pits, a surface condition to be avoided in surgical instruments.

For the manufacture of other table or kitchen articles, such as forks, spoons or dishes, soft material capable of being cold worked easily is required. For such purposes two types of material are suitable, stainless iron or the chromium-nickel alloys of the "Anka" type described in the previous chapter. Except for articles such as carving forks, the prongs of which should possess a considerable amount of "springiness" necessitating the use of a harder material, the stainless iron should be quite low in carbon, e.g., 0.10 per cent. or thereabouts, but a fairly high chromium content, e.g., 14 per cent., is preferable. Such material does not air-harden to any great extent and therefore troubles which might arise in the working of the material, due to this cause, are eliminated. The high chromium content is also desirable in order that the material may have very considerable resistance to corrosion even when annealed or more or less cold worked.

With regard to carbon content, it is of course true that material containing a considerably greater amount of this element than stainless iron may be made very soft by annealing, probably sufficiently soft to enable the necessary cold work to be carried out on it in many cases. Such

annealed higher carbon material, however, is distinctly less resistant to atmospheric corrosion than stainless iron of approximately the same or lower hardness, a condition of affairs readily understandable from the remarks in Chapter V.

Polished table articles, such as spoons and forks, when made of stainless iron, have one characteristic which may or may not be a disadvantage according to personal tastes. When compared with polished silver or some of the non-ferrous alloys used for similar purposes, they have a distinct bluish tint, especially if chromic oxide has been used as a polishing medium. This colour effect, which may be modified to some extent by using rouge instead of chromic oxide as a polishing powder, can be noticed quite plainly when such stainless iron articles are placed side by side with polished silver articles. Whether this colour effect is a disadvantage or not is purely a matter of taste, but for those who dislike it, a remedy is available in the use of the chromium-nickel alloys of the "Anka" type. Polished articles of these alloys have a distinctly yellowish tint, especially if they have been polished with rouge, and hence they do not contrast so strongly with silver or alloys of the "German silver" type. Here again a soft material is required for ease in pressing or other cold working operations; one such as "Anka" type "A" (page 229), having a tensile strength when softened of about 40 tons per square inch, would appear to be suitable. Compared with the non-ferrous alloys generally used for such purposes, all types of stainless material are comparatively hard; it is obviously an advantage, therefore, to use as soft a type of this material as is available. The remarks in the previous chapter as to the hardening effect of cold work on the austenitic steels and to the use of fully austenitic material (see page 240) should also be borne in mind.

In point of chronological development, probably the next outlet of any commercial importance for stainless steel, after that of cutlery, was for the manufacture of valves for aeroplane engines. During the war, the output of material for this purpose was large; since that time, for obvious reasons, the demand has been less, though the steel has been used to some extent for valves for other internal combustion engines. The requirements for a satisfactory valve material differ widely from those for material in which resistance to

corrosion is the all-important feature. For valves, strength at high temperatures and resistance to erosion and oxidation while hot are of prime importance. To this end, a rather higher carbon content than is usually found in stainless material is of value and, as pointed out in an earlier chapter (see page 224), there is no necessity to use a very high content of chromium. It is interesting to recall, in this connection, that the valves used in the engine of the first aeroplane to fly across the Atlantic were manufactured from the chromium-silicon steel (made by Messrs. Brown Bayley's Steel Works, Limited), containing about one per cent. of the latter element, the properties of which are described on page 224.

In selecting a particular type of steel for the manufacture of some particular valve, the temperature likely to be reached in service by the head of the latter is a determining factor. The hotter a valve gets, other conditions being equal, the greater the necessity for selecting specialised types of material for its manufacture.

One of the most important engineering uses of stainless steel is in connection with hydraulic and steam service work. Much of the development in this direction is due to the work of the author's colleague, Mr. F. G. Bell, Chief Engineer at Messrs. Brown Bayley's Steel Works, Ltd., whose enthusiasm for the use of the material in overcoming difficulties in maintaining service, due to the failure of other types of metal, has been a steadily increasing quantity.

The advantages of stainless steel as compared with gun-metal, nickel-copper and other alloys for valves and rams is now recognised by many engineers, so that it is not necessary to enumerate all the suitable applications of the metal. It will probably be sufficient to describe a few typical examples and enlarge upon the points to be observed in substituting stainless steel in place of the metals in general use in the past.*

The present year (A.D. 1925) has been notable in the engineering world as being the railway centenary; it may not be amiss, therefore, if the locomotive be taken as an example which offers suitable opportunities for testing the

* An account of some of the earlier experiences in using stainless steel in connection with steam and hydraulic service was given by Mr. Bell in an article "Stainless Steel" in the *Iron and Coal Trades' Review* for August, 10th, 1923. A shorter account was also given by the author in a paper before the Cleveland Institution of Engineers (Proceedings, March 5th, 1923).

properties of stainless steel in connection with steam service.

For the past two or three years several locomotives have been in continuous service fitted with the stainless steel parts enumerated in Table XXXV ; it will be of interest to record the behaviour of these several parts. At the outset, it may be said that generally speaking it has not been necessary to "grind-in" any of the valves during this period.

TABLE XXXV

Stainless Steel Parts fitted to Locomotives.

- | | |
|---|--------------------------------|
| 1. Safety valves. | 8. Regulator valves. |
| 2. Feed-check valves. | 9. Water gauge fittings. |
| 3. Steam whistle valves. | 10. Pressure gauge valves. |
| 4. Steam brake valves. | 11. Injector cones and valves. |
| 5. Steam jet valves. | 12. Steam distribution box. |
| 6. Blow-off cocks. | 13. Piston rods. |
| 7. Injector valves, steam
and water. | 14. Valve rods. |
| | 15. Brake rods. |

General experience with locomotive safety valves made of gun-metal or bronze indicates that they require "grinding-in" about every month or so. No definite comparison can be made on this score with regard to the stainless steel safety valves tried, for the simple reason that they have not yet, after three years' service, required attention of any description. One may safely say, however, that the balance in their favour is at least thirty to one.

Three types of stainless steel safety valves are shown in Fig. 101 and in each case the seating is simply pressed into the cast-iron or cast-steel valve body. Should a bronze body be used as container for the valve, however, it is necessary to screw the seating in or else make a rigid attachment by means of bolts, otherwise, owing to the co-efficient of expansion of stainless steel being much less than that of bronze, as indicated in Fig. 74 (page 144), the seating would become loose when hot and lift with the valve, making the latter inoperative.

Stainless steel valves and seats may be machined from forgings or drop stampings or from a rolled bar ; either of these methods is preferable to that of using castings. The latter are likely to be less sound than the forged or rolled

a little softer than the valve and to let the face of the valve cover and overlap the face of the seating; by so doing, the valve face is not marked or grooved by the pressure between the two faces. Stainless steel is adaptable in this respect owing to the ease with which its hardness may be modified. Experience has suggested that a suitable method is to harden and temper the seatings so that they have a Brinell hardness number of about 270, a value obtainable from a stainless steel, containing about 0.30 per cent. carbon, after hardening and then tempering at about 600°C. For the valve itself a considerably higher Brinell hardness number is suitable, e.g., about 370 to 400, such as would be obtained by air hardening a similar, or somewhat milder, steel followed by tempering at 300°/500°C. The seatings with their lower hardness, may be finish-machined after they have been heat treated. The harder valves are rough machined prior to final heat treatment, while the steel is in the softened condition. They are then heat treated to give the required hardness value, pickled to remove scale and then machine-ground on the working faces.

Owing to stainless steel being highly resistant to wear and erosion, the machine-grinding of articles made from it may be found to be somewhat troublesome; if, however, the wheel is kept in perfect condition and a suitable grit and grade selected, excellent results as regards the finish of the article may be obtained. The type of wheel required varies to some extent with the machine and the work but for a heavy rigid type of machine such as a Norton plain grinder, a 24 combination M. Vitrified wheel has been found suitable for roughing work and a 24 combination L. Vitrified wheel for very fine work. Equally good results may be obtained by the use of a 46 combination M or L. Vitrified wheel on a light universal grinder.

All the remarks on safety valves apply with equal force to feed-check valves. Fig. 102 shows several designs of such valves which have given excellent results when made of stainless steel. The experience gained with these valves tends to show that when made as indicated above, they will run for years without "grinding-in" but it is obvious that sooner or later they will require some attention in this respect. Apart from this, however, it sometimes happens that a seating is distorted while being fixed in the valve body,

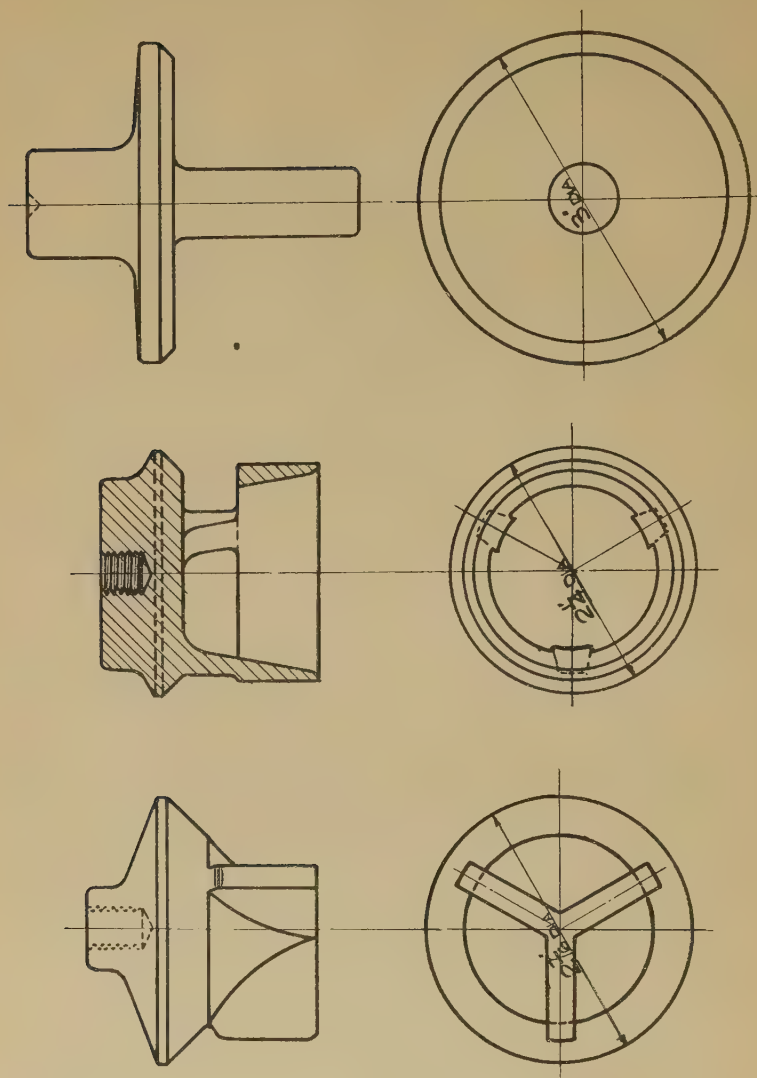


FIG. 102. Stainless Steel Boiler Feed-Check Valves as used on Locomotives.

thus necessitating "grinding-in." In such cases, the faces of the valve and seating should be smeared with a small amount of fine carborundum paste and then the two lightly ground together by hand. Only the lightest pressure should be exerted and after two or three turns, the faces should be cleaned. If these precautions are taken, the operation is simple and sure but if too much pressure is exerted or the

faces are not regularly cleaned, the metal is likely to seize and tear, leaving a rough surface difficult to deal with.

The various steam stop valves on a locomotive are dealt with in a similar manner to those already described but a word with regard to spindle packings may be useful. It was mentioned in Chapter V that if stainless steel and graphite are in contact while immersed in certain electrolytes, electrochemical effects are liable to be set up which will produce pitting in the steel. A similar action is also liable to occur if the graphite and steel are in contact in a damp atmosphere such as is characteristic of a great part of the year in this country. If the packing used for steam stop valves consists simply of graphited asbestos, pitting of the spindle where it is in contact with the packing is very liable to take place. The liability of this occurring is reduced by using steel with a high chromium content, but even with steel containing 15 per cent., it is not entirely removed. The chromium-nickel steels of the "Anka" type, however, do not appear, as far as experience goes, to be attacked under such conditions and if the use of such a type of packing is essential it would be preferable to make the spindles of this steel. The trouble, however, may be avoided by the use of a greasy, graphited asbestos packing; in this case, ordinary stainless steel works perfectly satisfactorily. The use of such lubricated packing would appear to be preferable in all cases, irrespective of what metal is used for the spindle as there is a sliding action between this and the packing and lubrication would seem to be necessary on this ground alone.

In passing, the results of some recent tests on packing materials may be cited as bearing on the point raised above. For these tests, which were carried out over a period of three years, two similar "Weir" pumps were used; in one of the pumps, carbon steel was used for the steam piston rod and, in the other, stainless steel, similar packing being used in both cases. The tests were primarily carried out for the purpose of noting the relative wear of the two steels, the tests on the various packing materials being a secondary consideration, but they showed that the type of packing used was of considerable importance inasmuch as it influenced not only the amount of wear on the rods but also the relative efficiency of the stainless steel.

When a greasy graphited asbestos packing was used,

the amount of wear of the carbon steel rod was five times that of the stainless steel; on substituting a rubber asbestos packing the ratio rose to 56 to 1 while when use was made of a packing composed of rubber, asbestos and white metal and having a wearing face consisting largely of the white metal, the ratio was 8 to 1. The actual amount of wear of the stainless steel during similar periods with the different packings was about the same, the loss in diameter being about 0.0005 inches in all cases. The carbon steel, on the contrary, was extremely sensitive to the type of packing used, the amount of wear of these rods during similar periods varying between 0.0025 and 0.0140 inches.

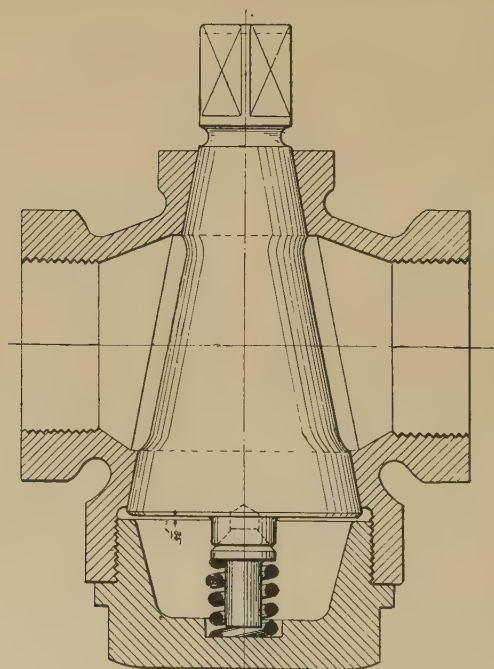


FIG. 103. 2" Steam Plug Cock fitted with Stainless Steel Plug.

Stainless steel plugs working in gun-metal bodies make a good combination for blow-off cocks or water gauge fittings although the gun-metal is liable to be attacked in time with certain types of water. Fig. 103 shows a suitable design of blow-off cock made as suggested above, which has been thoroughly tested. The water gauge fittings illustrated

in Fig. 104, which similarly consist of stainless steel plugs fitted into gun-metal bodies, are also noteworthy in that the use of packing has been entirely done away with. Water gauge fittings of this type have been in use for nine months or so and have not yet needed any attention. An important

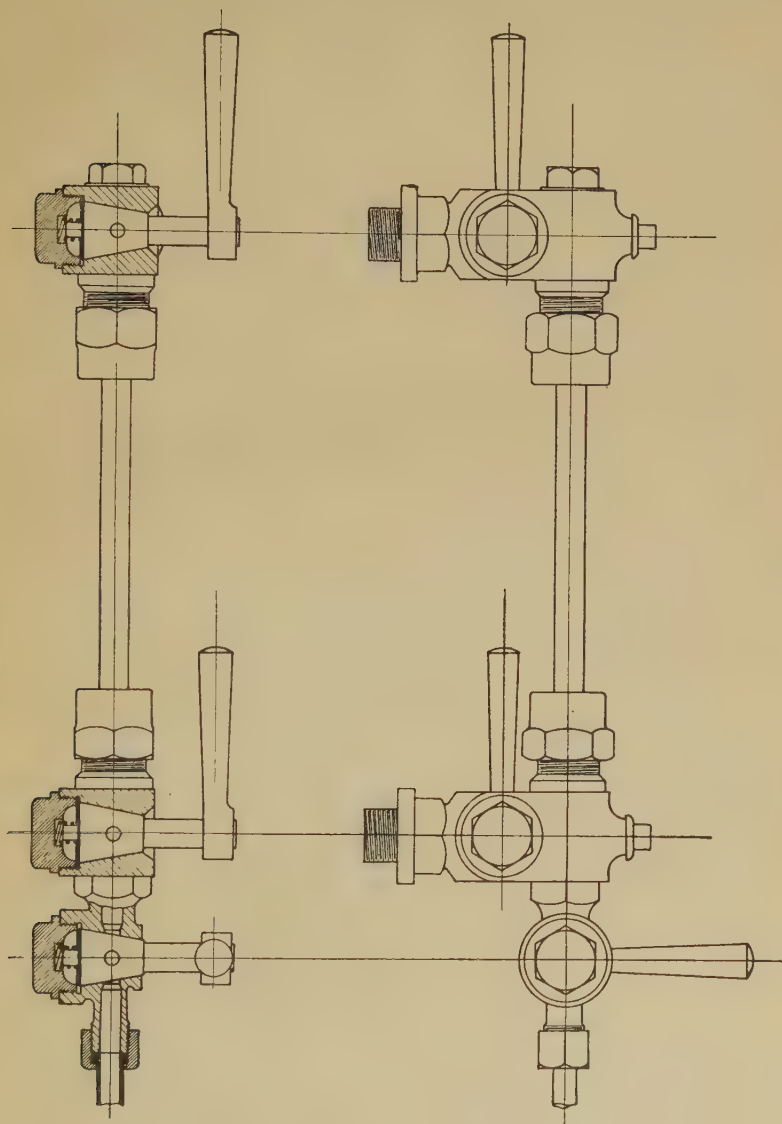


FIG. 104. Locomotive Water Gauge Columns fitted with Stainless Steel Plugs.

point which must be watched when designing stainless steel plugs for use in gun-metal bodies, is in regard to the taper of the plug. This must be at least 1 in $2\frac{1}{2}$ if the cock is to be used for hot work ; a smaller taper will result in the plug binding in the body when the two cool down, due to the difference in the rate of expansion of the metals.

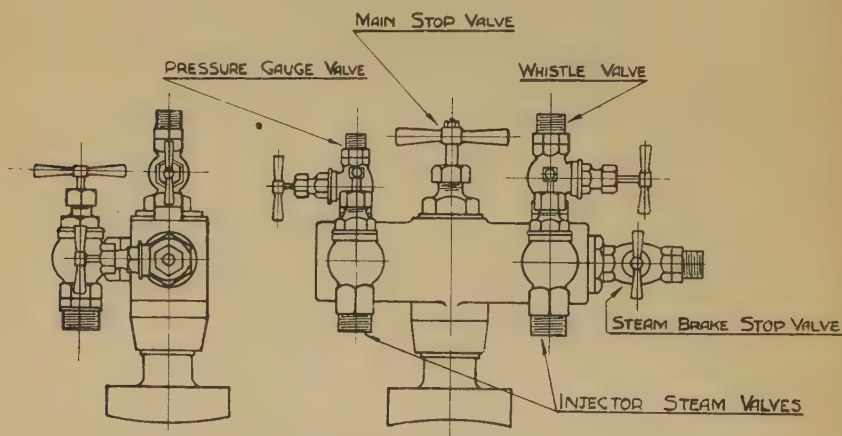


FIG. 105. Stainless Steel Steam Distribution Box with Valves, as used on Locomotives.

Fig. 105 shows a neat arrangement of a locomotive steam distribution box, the whole of which—box, valves, seats and spindles—has been made of stainless steel. The box is machined from a mild stainless steel forging, containing 0.15 to 0.20 per cent. carbon, hardened and tempered to give a tensile strength of 40/50 tons per square inch. The valves and seatings are made as described earlier. The spindles, if made each in one piece with its corresponding valve, will perforce be made of the same steel as the latter ; if, however, the valve is made as a separate piece which is screwed on or otherwise attached to the spindle, the latter is preferably made of mild stainless steel, e.g., containing 0.10 to 0.15 per cent. carbon, or if non-greasy graphited packing be used, “Anka” steel may be substituted as described earlier in this chapter.

It is well known that when two pieces of steel are rubbed together, there is a distinct tendency for the surfaces to tear or seize. This probably accounts for the fact that in certain

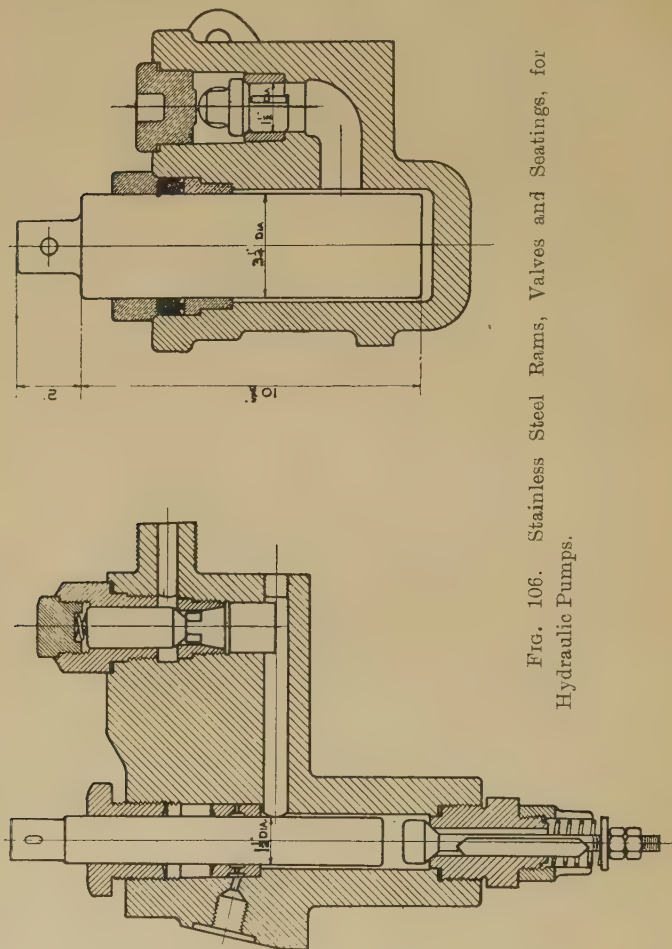
cases where stainless steel discs and seats have been used in valves of the parallel flow type, the faces have become scored or rough. This tendency to seize can be mitigated by making both the discs and seats as hard as practicable, for example, 400/450 Brinell hardness number, but generally speaking it is advisable in valves of this type to make the seating of hardened stainless steel and the disc of a good nickel-copper alloy, e.g., one containing about 55 per cent. nickel and 35 per cent. copper (the remainder consisting of smaller amounts of tin, iron, zinc, etc.); with such a combination there is little or no tendency to seize. In this type of valve, the erosive attack is much more severe on the seating than on the disc, the latter being out of the path of the steam when the valve is fully open; hence the more resistant metal, stainless steel, should be used for the seating and the softer nickel-copper alloy for the disc rather than vice versa.

The benefits resulting from the intelligent use of stainless steel parts are equally evident in hydraulic work. Actually this was recognised some years before the use of stainless steel for steam valves was thought of; a result probably due to the fact that steel works are amongst the largest users of hydraulic power and were thus likely to suffer from the failure of the metals, previously obtainable, to stand up to the severe demands made upon them. It is a fact that either late in 1913 or early in 1914, three large stainless steel rams were fitted to a forging press pump in a Sheffield steel works and to-day, twelve years later, the rams are still in service.

Fig. 106 illustrates two types of hydraulic pump bodies with stainless steel rams and valves, the latter and the corresponding seats being made in a similar way to that described for steam valves and seats.

Stainless steel rams should be rough machined from forgings or rolled bars in the softened (i.e., fully tempered, or annealed) condition, a suitable analysis of material being about 0.25 per cent. carbon and about 14.0 per cent. chromium. The rams should then be hardened, followed by tempering at 300°/400°C., so as to give a Brinell hardness number of the order of 400. The ram is then re-tempered, at the small end only, in the range 600°/650°C. so as to reduce the hardness at this point to a Brinell number of about 250/270. The extra tempering of the small end allows this

part to be finished in the lathe and drilled or milled as required; in addition it has the effect of toughening the article at its weakest point. The barrel of the ram, being hard, must be finished by grinding; as this should be done with all rams and



rods, whatever the material used for making them, no inconvenience is caused by this necessity. The resulting ram will have, under ordinary working conditions, a life far in excess of that to be expected by the use of any other known metal. As an illustration of this it may be stated that a $3\frac{1}{4}$ -in. ram of the design shown in Fig. 106, worked for two

and a half years with water at a pressure of 850 lbs. per square inch and was then reduced in diameter by 0.005 inch only ; at the same time the average life of the leather " U " packings was nine months.

The abnormally long life of " U " leather packing when used with stainless steel rams is one of the outstanding features of the use of this material and leads to very considerable economies in the upkeep of hydraulic appliances. That lessened wear on the leathers would be found is understandable, because the hard stainless steel ram takes a high polish and retains this polish in use ; owing to its hardness it is not easily scored. The actual increase in life of the leathers, however, is considerably greater than would have been anticipated.

The economies obtainable by the use of stainless material do not reside solely in the increased life of the articles made therefrom or in the cost of leather packings, however, though these are often considerable items. Still greater savings are brought about by the reduction in loss of time due to stoppages. This, of course, applies to other applications of the material both in hydraulic and steam service work. The author remembers particularly one case which occurred at Brown Bayley's Steel Works Ltd., and which will serve as an example. During the war period a phosphor bronze valve in connection with a 1,200-ton forging press was constantly giving trouble. It required " grinding-in " every three weeks and although this was done regularly, troubles leading to stoppages were of frequent occurrence. At this period stoppages were particularly obnoxious and moreover very costly ; in this particular case it was estimated that the loss due to stoppages was of the order of £1 per minute. A stainless steel valve was fitted and during the next two years the valve never required any " grinding-in " and no stoppage due to valve trouble occurred.

The benefits likely to accrue from the use of stainless steel for the blading of turbines were realised some years ago and already sufficient experience in this direction has been obtained to show that the performance of this material justifies expectations.

The conditions arising in different types of turbines vary considerably, so much so that the most desirable physical properties required in the material for blading differ

appreciably in the several types of turbine. It may be useful to consider briefly some of these variations.

In turbines of the impulse type, the vanes in the nozzle diaphragms are often made from plate or strip, bent to the necessary shape. They are fixed in position by casting the iron diaphragm round them. This method of preparation demands certain properties in the material used for making vanes. The sheet must be soft and not springy, so that it may easily be pressed into shape and, when so pressed, will take accurately the shape intended. The method of making the diaphragm, by casting round the vanes, demands that the material used for the latter shall not air harden to any great extent. During the casting operation the vanes, which have been previously inserted in position in the mould, are heated up to above the fusing point of cast iron, approximately $1,150^{\circ}$ to $1,200^{\circ}\text{C.}$, and afterwards they cool down more or less rapidly depending on the size of the diaphragm. If the material hardens to any great extent under this treatment, the vanes will be comparatively brittle, more particularly close to the point where they enter the cast iron centre or rim. The requisite properties are obtained in a satisfactory manner by the use of mild stainless steel or stainless iron containing 0.10 or 0.15 per cent. carbon; sheets of such material, when fully tempered are easily pressed to shape and they do not harden unduly when "cast-in." The latter point may be illustrated by a series of tests carried out to show the influence of carbon content on this requirement. Strips about 6-ins. long, 1-in. wide and $\frac{1}{16}$ -in. thick, of steels containing respectively 0.10 per cent., 0.15 per cent., 0.18 per cent., 0.21 per cent. and 0.3 per cent. carbon were embedded in blocks of cast iron about 12-in. \times 3-in. \times 4-in. The blocks were cast round the strips, the latter being placed in the moulds in such a position that a length of two inches of each was embedded in the cast-iron as indicated in Fig. 107. After casting, the blocks were allowed to cool down in the normal manner for castings of such size. Prior to "casting-in," the strips had all been hardened and fully tempered in order to put them into a tough ductile condition. After the castings had become quite cold, the projecting ends of the strips were bent through 90° at the point where they emerged from the block, as indicated by the left-hand strip

in Fig. 107. All the strips of the samples containing 0·18 per cent. carbon or less stood this test successfully. Some of the strips containing 0·21 per cent. carbon also bent successfully, but the others broke, while none of the strips containing 0·3 per cent. could be bent through 90° without breaking. From these results, a carbon content of not more than 0·18, or better 0·15, per cent. would appear to be desirable in the stainless material used for vanes treated in such a manner. The lower limit is preferable as a measure of safety because the air-hardening capacity of the steel is affected also by its chromium and nickel content.

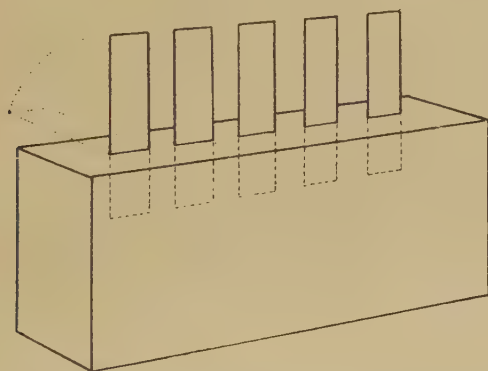


FIG. 107. Cast Iron Block and Stainless Steel Strips used for testing the effect of "Casting-in" on the hardness of the steel. See page 278.

It will be understood, of course, that the intensity of the air-hardening effect produced in the blades will depend on the size of the diaphragm casting and the speed with which it cools. Reference to Fig. 18 (page 35), however, will show that an ordinary stainless steel containing about 0·3 per cent. carbon, when heated to temperatures in the neighbourhood of 1,200° C. or over, may be cooled therefrom at comparatively slow rates and still be hard. It is possible, of course, that the rate of cooling of a large diaphragm casting might be sufficiently slow to prevent any air hardening effect in the inserted stainless steel blades, no matter what amount of carbon these contained. It may be asked whether in these circumstances the use of low carbon material for the blades is essential. After such a slow cooling from temperatures in the neighbourhood of 1,200° C., all stainless steels, except

the mildest, possess a coarse structure of pearlite together with more or less free ferrite or carbide, depending on the carbon content, similar to those shown in Figs. 2, 3, 4 and 21. The mechanical properties associated with such a structure are not particularly good and, as was shown on page 101, they are adversely affected by increasing the carbon content. It would appear, therefore, that even when the cooling conditions are likely to be such as would not produce any air hardening effect in the inserted blades, it is advisable to use the lower carbon material on account of its relatively better properties under such conditions. It may be concluded, therefore, that the most suitable stainless material for the manufacture of the vanes in the nozzle diaphragms of impulse turbines is that containing not more than about 0.15 per cent. carbon.

For the moving blades of such turbines, however, the conditions are quite different. Such blading is generally short and sturdy and there is not a great deal of it. Consequently the blades are generally milled from heat-treated bars or forgings of suitable size and then secured in their proper positions by various mechanical devices. The steel may, therefore, be harder than that used for the nozzle diaphragm, so long as it is machineable, and there is no reason why it should not air harden. Hence, unless there are any manufacturing details in connection with the blades which would make a softer material preferable, a steel which will give a tensile strength of about 45 to 55 tons per square inch would appear to be suitable for such blades. Owing to its greater hardness, it would probably resist erosion better than the very soft material.

In turbines of the reaction type, the conditions are not so severe as in the impulse type; possibly owing to this the makers of such turbines did not take up the use of stainless steel as early as those who had to combat the greater erosion of the impulse turbine. In the reaction turbine, the blading is both narrower and thinner than in the other type and there is a great deal of it. Consequently such blading is generally cold rolled or cold drawn to shape. Many of the blades are also very long, hence the material used for them should be tough. The ends of the blades are generally brazed to shrouding wires while the longer blades are given further rigidity by being brazed to other

shrouding or lashing wires in one or more places along their length.

The general practice of cold rolling or cold drawing the blades makes the use of a fairly soft material desirable and for such purposes stainless steel or iron containing about 0.20 per cent. carbon or less, hardened and tempered to give a tensile strength of 35 to 45 tons per square inch would appear to be suitable. The advisability of using a low carbon material, however, is still more evident when one considers the effect on the blades of the numerous brazing operations needed to fit the shrouding wires. This point was considered in an earlier chapter (see page 74) where it was shown that although brazing could be carried out at temperatures lower than the Ac.1 point of stainless steel if a suitable brazing mixture were employed, it was better to use low carbon stainless material in preference to that of higher carbon content for purposes involving brazing as a measure of safety, because the bad effects of an accidental overheating during the brazing operation were considerably less severe in the case of the lower carbon steel than the other. It will be understood that although it is possible to carry out the brazing operation, using the special brazing alloys mentioned, so that the temperature of the steel never exceeds about 800°C., the Ac.1 point of stainless steel, this operation demands very great care, so much so that it is very likely under ordinary workshop conditions, such as obtain in the brazing of shrouding wires, the thin edges of the blades will be heated above this temperature. It is in these cases that the value of stainless iron is very evident. The higher carbon stainless steel acquires an appreciable air hardening capacity almost as soon as it has passed through the Ac.1 change; on the other hand, stainless iron does not air harden to any great extent until heated to considerably higher temperatures (e.g., 900° or 950°C.) and even then the intensity of hardness produced is, of course, much less than in the higher carbon steel, particularly if the chromium content is fairly high, e.g., 13 or 14 per cent. As a result of this, the brazing temperature of stainless iron may be raised considerably above that likely to cause hardening in the higher carbon steel, without producing any noticeable hardening effect in the lower carbon material. The advantages of this distinctly greater latitude in the

brazing of the low carbon material will be evident to those who, from practical experience, know the difficulty in controlling the maximum temperature reached by thin strips of metal when heated by a blow-pipe flame.

For most of the blading of such turbines, low carbon material, hardened and fully tempered to give a tensile strength of about 35 to 40 or 45 tons per square inch appears to be suitable. Sometimes, however, erosion is found to be rather more severe at the inlet end of the turbine than at other places and so the first few rows of short blades are in some cases made of somewhat harder material, having a tensile strength of about 45 to 55 tons per square inch. Material of this hardness may be obtained from suitable low carbon material by hardening followed by tempering at 600°C. (see Table II, page 83).

In some cases instead of brazing a shrouding ring to the tips of the blades, the latter are passed through slots in the ring, which is often made of stainless steel strip, and then the tips rivetted over cold so as to form a tight fastening. Such a method is also used for connecting up the ends of the moving blades of impulse turbines. There is usually no difficulty in forming satisfactory connections by thus rivetting the tips of the blades if the latter have a tensile strength of not more than about 50 tons per square inch. Should any trouble be experienced with the rivetting of hard blades, it is quite feasible to soften locally the tips of these, particularly if they have been made in the manner suggested in the preceding paragraph.

The general trend in engineering work is towards the use of steam at higher temperatures and pressures; already one hears of temperatures of 800°F. together with 550 lbs. pressure while 1,000°F. has been suggested; such a temperature would permit an absolute pressure of 2,000 pounds per square inch together with some 360 degrees of superheat. It is possible that with such conditions of temperature and pressure ordinary stainless steel may not be sufficiently resistant to the erosive action in the turbine. If this should prove to be the case, it is probable that the use of the special nickel-chromium alloys described in the previous chapter, possibly modified by the addition of other metals such as tungsten or molybdenum, will enable these severe erosive conditions to be withstood. Still more severe

conditions will without doubt be encountered should the gas turbine ever emerge from the experimental stage to successful practical application and one may well believe that the metallurgist will be taxed with a most difficult problem in providing alloys to withstand successfully the conditions likely to be met with in such a turbine.

In addition to the application of stainless steel in solving some of the problems met with in such distinct types of engineering work as steam and hydraulic service and turbine manufacture, there are many occasions arising in engineering or steel works where the use of stainless steel for some machine detail would result in a considerable saving, at least of trouble. For example, in the manufacture of railway tyres the steel for these is frequently cast in long ingots which are subsequently cut up, in powerful lathes, into blocks of the necessary size. In two such lathes in use at the works the author is connected with, the tool holders are fitted with bolts, nuts and traversing pinions made of stainless steel; by so doing much trouble due to the rusting of similar parts made from ordinary steel, causing them to stick, has been avoided. In the same way, the main saddle taper wedges for the same lathes when made of ordinary steel were found to corrode at both ends, forming barrel-shaped wedges which caused the saddle to rock when the machine was at work. This has been avoided by making these parts of stainless steel.

As will be gathered from the short account given in Chapter VI of the action of specific reagents on stainless steel, this material is not a universal panacea for all the corrosion ills and troubles which the chemical engineer meets with in his work. In certain directions the use of stainless steel has proved of great value to him; in others its use is not likely to be attended with any great success. It may be of some assistance to him if examples of the application of stainless material are quoted.

The advantages likely to be obtained by the use of stainless steels for the construction of plant for the manufacture and handling of nitric acid have already been mentioned. Complete immunity from the attack of this acid is obtained with stainless iron having a high chromium content (not less than about 15 per cent.) or with the chromium-nickel alloys of the "Anka" type containing a similar

or greater amount of chromium together with sufficient nickel to make them completely austenitic. Which of these two alloys is preferable under given conditions depends on circumstances. The stainless iron is somewhat cheaper than the austenitic alloy and on that account has advantages where large quantities of sheets are required, as in the construction of towers. The cold rivetting of such sheets is also more easily carried out if the rivets are made of stainless iron, as was mentioned in the last chapter.

It may also be noted that, as a whole, stainless iron is more easily machinable than the austenitic alloy although trouble with the latter is only likely to occur if certain precautions are not taken. These are connected with the capacity of the steel for work-hardening. It is essential in machining such austenitic alloys that a sharp tool, cutting freely all the time, be used. If the tool grinds along the surface without cutting, a hardened skin will form which will make further cutting difficult or, indeed, almost impossible. For this reason trouble is likely to occur, for example, when drilling long holes, because the point of a drill grinds rather than cuts. It is also advisable to use a centre punch lightly; if used heavily, the succeeding drilling of the centre hole is likely to give considerable trouble. These precautions are especially important with alloys which contain barely enough nickel to be fully austenitic, because such alloys work-harden rapidly; also they obviously apply more particularly to alloys with a high tensile strength than to those having a lower value for this property.

It cannot be said that any of the stainless alloys which have been described are really resistant to sulphuric and hydrochloric acids. A good degree of resistance to the attack, at atmospheric temperatures, of dilute solutions of these acids can certainly be obtained by the use of the special alloys described in Chapter VII, but if the temperature of the acid be raised, the rate of attack generally increases rapidly. An exception to this is found with the complex chromium-nickel-molybdenum alloy (see page 257) which appears to resist the attack of dilute sulphuric acid even when hot and will probably prove of value when such conditions have to be met. Where, however, slightly acid liquors at about atmospheric temperature have to be pumped or otherwise handled, the use of the chromium-nickel alloys,

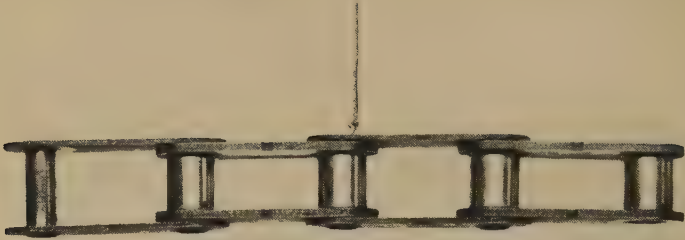


FIG. 108. Part of stainless iron chain after running for the duration of a crushing season in a "Juice Strainer."—see page 285.

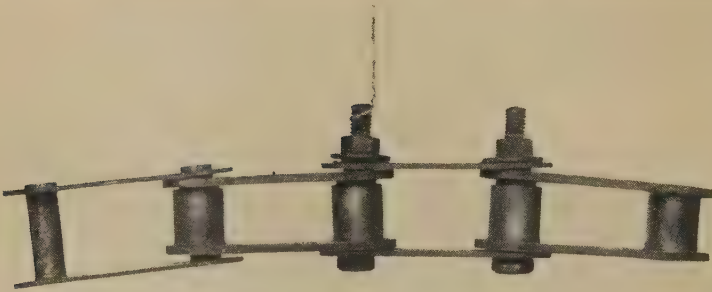


FIG. 109. Part of ordinary steel chain which ran alongside the stainless iron chain shewn in Fig. 108,

[To face page 285.

either the "Anka" type and or that containing about 25 per cent. of nickel, would appear to have advantages for the construction of machinery handling such liquors.

A probably greater field of usefulness for the various types of stainless steel will be found in the handling of the various organic acids or of the weaker mineral acids. In some cases use may be made of ordinary stainless steel or iron, in others of the special chromium-nickel steels such as "Anka"; in this connection the data already given in Chapters VI and VII may be referred to.

Still greater opportunities occur in the handling of salts and other more or less neutral bodies, either inorganic or organic, which constitute so large a part of the "heavy chemical" industry. It is not necessary to give any detailed suggestions as to the possibilities in this direction; they may be illustrated, however, by the result recently obtained from the use of a stainless iron chain in a Juice Strainer in the sugar industry. Such chains are usually made of ordinary steel and they give considerable trouble owing to corrosion and rapid pitch extension. Two such chains, which have the form shown in Fig. 108, were installed side by side and ran for the duration of a crushing season. One chain was made of ordinary carbon steel, the studs, bushes and rollers being case-hardened; the other was made entirely of stainless iron. After the season's work the stainless iron chain was found to have scarcely suffered; the ordinary steel chain on the other hand was unfit for further use; in fact, bolts had to be inserted in the hollow studs to hold the side plates together in order that the chain might run to the end of the crushing season. This is evident from the photographs, Figs. 108 and 109. These show a short length of each chain at the end of the season's work; each piece is suspended by the middle joint and one can see that whereas the joints of the stainless iron chain are still in good condition, those of the ordinary steel chain are very loose and are only held together by the inserted bolts which are themselves appreciably corroded.

For many engineering purposes, in connection with which the relative incorrodibility of stainless steel would seem to offer advantages, it is not really essential that the appliance made from it should be absolutely unattacked under working conditions. Such a degree of resistance

is certainly the ideal, and it is probable that in many cases one or other of the numerous forms of stainless steel would approximate to this condition. If, however, the rate of corrosion of the stainless steel appliance or plant is so much slower than that of similar parts made of ordinary steel (or other metals) that the increased life of the stainless article more than compensates for its generally greater initial cost, as compared with the other metals, the use of stainless steel will obviously effect economies. In the case mentioned above, against the greater initial cost of the stainless iron chain should be set the comparative freedom from the trouble and inconvenience caused by the frequent renewal of corroded parts of machinery which is required to handle in a limited time, large quantities of a natural product, particularly as this product must be dealt with as expeditiously as possible after it is ripe, otherwise its value may depreciate considerably. It appears to the author that the greatest engineering uses of stainless material will follow on conditions such as those outlined above. It is scarcely probable that the cost of any type of stainless steel will ever become as low as that of ordinary steel or even approach this value. Its cost to the engineer, however, should be judged by its service and so long as this relative cost in terms of service is considerably lower than that of ordinary steel, its use will prove advantageous to the engineer, chemical or otherwise, even though the machinery made from it be not perfectly immune from attack.

APPENDIX

APPENDIX

The texts of the Canadian and United States Patents for the manufacture of Stainless Steel are as follows :—

I. CANADIAN PATENT—No. 164,622, August 31st, 1915 (application dated April 21st, 1915).

TO ALL WHOM IT MAY CONCERN :

Be it known that I, HARRY BREARLEY, of the City of Sheffield, County of Yorkshire, England, Metallurgist, having invented certain new and useful improvements in the process of producing MALLEABLE STEEL, do hereby declare that the following is a full, clear and exact description of the same.

My invention relates to the production of steel or steel alloys and has for its object to produce a malleable steel which shall be practically untarnishable and can be forged, rolled, hardened and tempered under ordinary commercial conditions. The invention results from the discovery that the addition of certain percentages of chromium and carbon to iron will produce a steel having the characteristics above referred to. I have discovered that the addition to iron of an amount of chromium anywhere between nine (9) and sixteen (16) per cent., and also an amount of carbon not greater than seven-tenths per cent. (0·70 per cent.) will result in such a product. In this product there are no microscopically distinguishable free carbides.

I have further found by experiment that steels containing less than eight per cent. (8%) of chromium are relatively tarnishable whatever the amount of carbon that they contain up to the limit at which they are malleable and can be hardened and tempered. I have also found that when the amount of carbon exceeds seven-tenths per cent. (0·70%) the polished steel is tarnishable whatever the amount of chromium it may contain and that this condition corresponds with the appearance in the steel of free carbides

which are distinguishable microscopically on polished and etched specimens.

A typical composition for the untarnishable steel embodying my invention would be as follows: carbon 0·24 per cent.; manganese 0·30 per cent.; chromium 13·0 per cent.; iron 86·46 per cent. In producing such steel embodying my invention I preferably use an electric arc melting furnace. It can be readily made in such a furnace. It forges easily into sheets or strips such as are required for knife blades, for example, and can be hardened and tempered by ordinary commercial processes. It is suitable also for structural purposes, the following being average mechanical properties after small bars of steel of the above composition have been oil hardened at 900° C. and tempered at 700° C., e.g. :—

Yield Point39 tons per square inch.
Maximum Stress		...48 tons per square inch.
Elongation25 per cent. on 2" × 0·564" test piece.
Reduction of Area		...63 per cent.
Izod Impact Figure		...86 foot lbs.

Steels which are otherwise of the same composition as the typical composition quoted above but containing greater amounts of carbon cannot be made so tough for any particular degree of hardness but they are suitable for purposes where great toughness is not required. Small amounts up to say one or two per cent. of Nickel, Copper, Cobalt and small amounts of Tungsten, Molybdenum and Vanadium appear to be without influence on the untarnishable property of the steel.

I am aware that claims have been made for alloy steels containing more than forty per cent. of chromium and nickel and for alloys consisting essentially of chromium and nickel or chromium and cobalt, and for alloys containing chromium associated with other elements but having now described the nature of my said invention I declare that what I claim is—

1. An alloy steel containing essentially from nine (9) to sixteen (16) per cent. of chromium and less than essentially seven-tenths per cent. (0·70%) of carbon.
2. A steel alloy containing chromium equal to at

least essentially nine per cent. (9%) and carbon to an amount not more than essentially seven-tenths per cent. (0·70%).

3. A malleable and temperable steel alloy containing iron, chromium and carbon, the iron being at least essentially eighty per cent. (80%), the chromium being at least essentially nine per cent. (9%) and the carbon being not more than essentially seven-tenths per cent (0·70%).

4. A malleable and temperable steel alloy containing chromium equal to at least essentially nine per cent. (9%) and carbon to an amount not more than essentially seven-tenths per cent. (0·70%), the balance being iron and less than essentially two per cent. (2%) of other metal.

5. A malleable and temperable steel alloy containing iron, carbon and chromium and the chromium being essentially from nine per cent. (9%) to sixteen per cent. (16%) and not containing essentially any microscopically distinguishable free carbides.

II. UNITED STATES PATENT—No. 1,197,256, Sept. 5th, 1916. (Application filed March 6th, 1916; continuation of application filed March 29th, 1915.)

TO ALL WHOM IT MAY CONCERN :

Be it known that I, HARRY BREARLEY, residing at Sheffield, Yorkshire, England, have invented a certain new and useful Improvement in Cutlery, of which the following is a full, clear and exact description.

My invention relates to new and useful improvements in cutlery or other hardened and polished articles of manufacture where non-staining properties are desired and has for its object to provide a tempered steel cutlery blade or other hardened article having a polished surface and composed of an alloy which is practically untarnishable when hardened or hardened and tempered. This alloy is malleable and can be forged, rolled, hardened, tempered and polished under ordinary commercial conditions.

The invention results from the discovery that the addition of certain percentages of chromium and carbon to iron will produce a steel capable of taking a polish and having the characteristics above referred to. I have discovered that

the addition to iron of an amount of chromium anywhere between nine per cent. (9%) and sixteen per cent. (16%), and also an amount of carbon not greater than seven-tenths per cent. ($\cdot 7\%$) will result in a product which, when made into knife blades, has the said characteristics.

I have further found from experiments that steels containing less than eight per cent. (8%) of chromium are relatively tarnishable whatever the amount of carbon that they contain up to the limit at which they cease to be malleable and capable of being hardened and tempered. I have also found that when the amount of carbon exceeds seven-tenths per cent. ($\cdot 7\%$) the polished steel is tarnishable whatever the amount of chromium it may contain and that this condition corresponds with the appearance in the steel of free carbids, which are distinguishable microscopically on polished and etched specimens.

A typical composition for the untarnishable steel blades embodying my invention would be as follows: carbon $\cdot 30$ per cent.; manganese $\cdot 30$ per cent.; chromium 13.0 per cent.; iron 86.4 per cent. In producing such steel I preferably use an electric arc melting furnace. It can be readily made in such furnace. It forges easily into sheets or strips such as are required for knife blades and can be hardened and tempered by ordinary commercial processes.

Knife blades embodying my invention are made from the steel above referred to being formed, hardened and polished by grinding or buffing in the ordinary manner, the product being a polished cutlery blade similar in appearance to other polished blades but possessing the remarkable quality of being practically untarnishable when subjected to the ordinary uses to which knife blades are subjected, because made from the alloy above described. My blades are tempered so as to be sufficiently resilient for ordinary requirements.

Small amounts, up to say one or two per cent. of nickel, copper, cobalt, tungsten, molybdenum and vanadium, appear to be without influence on the untarnishable property of the steel.

In practice it is best not to attempt to obtain an alloy containing above $\cdot 4$ per cent. of carbon, but rather to try to obtain an alloy containing an amount of carbon less than $\cdot 4$ per cent. thus leaving a wider margin for variations

from the alloy sought to be produced since the desired result is attained when considerably less carbon is present.

This application is a continuation of my application Serial No. 17,856, filed March 29th, 1915.

As is evident to those skilled in the art, my invention permits of various modifications without departing from the spirit thereof or the scope of the appended claims.

What I claim is—

1. A hardened and polished article of manufacture composed of a ferrous alloy containing between nine per cent. (9%) and sixteen per cent. (16%) of chromium and carbon in quantity less than seven-tenths per cent. (.7%).

2. A hardened, tempered and polished cutlery blade composed of a ferrous alloy containing between nine per cent. (9%) and sixteen per cent. (16%) of chromium and carbon in quantity less than seven-tenths per cent. (.7%) and not containing any microscopically distinguishable free carbids.

3. A hardened and polished cutlery article composed of a ferrous alloy containing between nine per cent. (9%) and sixteen per cent. (16%) of chromium and carbon in quantity less than six-tenths per cent. (.6%).

4. A hardened and polished article of manufacture composed of a ferrous alloy containing approximately carbon 0.30%, manganese 0.30% and chromium 13.0%.

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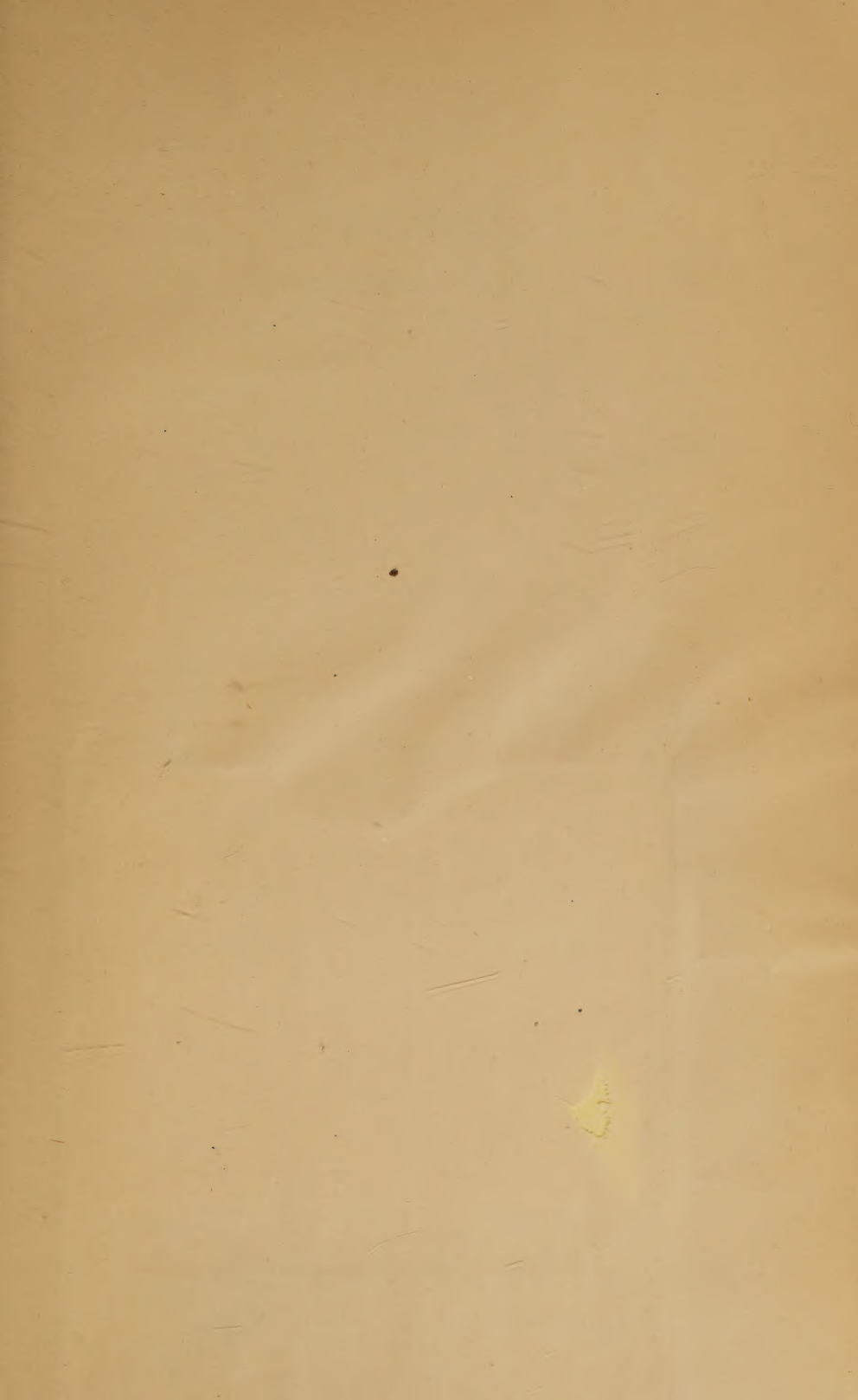
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